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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

2607. **A study of the reproducibility of analytical balances.** R. A. Johnson and C. B. Graham, jun. (*Anal. Chim. Acta*, 1955, **12** [5], 408–412).—The variation of rest-point reproducibility with variation of sensitivity adjustment is studied with three balances. At low sensitivities the reproducibility in scale units is constant; the reproducibility in mg units is limited by the readability of the scale, and can be improved by increasing the sensitivity or by replacing the scale with a micro scale and magnifier. When the sensitivity is increased over a certain limit, the reproducibility in mg is limited by the mechanical error of the balance and reaches a constant which is a criterion of the mechanical character of the balance. W. C. JOHNSON

2608. **Rapid weighing of electrodes with single-pan analytical balances.** I. Geld and I. F. Sternman (*Chemist Analyst*, 1955, **44** [2], 53–54).—Single-pan balances used for weighing large numbers of electrodes, crucibles, weighing-bottles, etc., can be tared with cut and numbered pieces of sheet-lead so that the wt. of (Pb + electrode) is a large integer, *e.g.*, 100 g. After the plated electrode (or crucible, etc.) is weighed, the wt. of the deposited metal (or other material) is read directly by disregarding the first digit. W. J. BAKER

2609. **Continuous weighing in gravimetric analysis.** Anon. (*Chem. Prod.*, 1955, **18** [5], 189–190).—The uses of the thermobalance in gravimetric analysis are discussed. Examples given are the determination of Cd and U, determination of magnesium and calcium oxalates in the presence of one another, and the assay of alloys of Cu and Ag. I. JONES

2610. **Aims and methods of trace accumulation.** H. Specker and H. Hartkamp (*Angew. Chem.*, 1955, **67** [6], 173–178).—The application of trace accumulation for quant. determinations for concentrations below measuring limits, or interference of main substance with test substance, requires processes leading not only to higher concentrations of trace elements, but also to increased differences between the concentrations of main and test substance. Preliminary treatments (purification of chemicals and digestion of test substance) and various methods of concentrating and separating main and test substance are reviewed and discussed (evaporation or extraction of trace or main substance, precipitation of traces, chromatography, ion exchange, electrolysis, etc.), with special reference to extraction and ion-exchange techniques. The importance of working with uncontaminated reagents is emphasised. (129 references.) S.C.I. ABSTR.

2611. **Nitrazine yellow solution as indicator for acid - base titrations.** W. Buss and G. Schmitt (*Lebensmitteltierarzt*, 1954, **5**, 56–57).—Methyl orange and nitrazine yellow (**I**) are compared and it is shown that **I** gives a much sharper end-point and much better results. A dilution of 1:10,000 of **I** is recommended. CHEM. ABSTR.

2612. **Ascorbic acid and Variamine blue in iodimetric determinations.** L. Erdey, E. Bodor and M. Pápay (*Acta Chim. Hung.*, 1955, **5** [3–4], 235–254).—Ascorbic acid (0·1 *N*) as the reducing titrant and Variamine blue (4-amino-4′-methoxydiphenylamine) as the redox indicator were compared with 0·1 *N* $Na_2S_2O_3$ and starch in a number of iodimetric determinations. Satisfactory results were obtained in the majority of cases. S.C.I. ABSTR.

2613. **Studies on derivatives of 8-hydroxyquinoline (oxine). The sensitivity and selectivity of 5-nitroso-oxine and 2-methyl-5-nitroso-oxine towards the group IIIB metals.** R. G. W. Hollingshead (*Anal. Chim. Acta*, 1955, **12** [5], 401–407).—The selectivity and sensitivity of 8-hydroxyquinoline and three of its derivatives as precipitants for $Al^{\cdots}$, $Y^{\cdots}$, $Ga^{\cdots}$, $In^{\cdots}$ and $Tl^{\cdots}$ are investigated. 8-Hydroxyquinoline precipitates all these metals; 8-hydroxy-2-methylquinoline precipitates all but $Al^{\cdots}$. With 8-hydroxy-5-nitrosoquinoline, pptn. occurs only with $Tl^{\cdots}$. 8-Hydroxy-2-methyl-5-nitrosoquinoline (prep. described) precipitates none of the metals. The increasing selectivity is attributed to the steric hindrance of the methyl group and the acidity conferred by the nitroso group. (See also *Anal. Abstr.*, 1955, **2**, 850.) W. C. JOHNSON

2614. **Salicylhydrazide: a reagent of wide use in organic and histochemical analysis.** B. Camber (*Nature*, 1954, **174**, 1107).—Salicylhydrazide condenses with aldehydes to give products having a brilliant fluorescence under u.v. light, whereas the ketonic derivatives show a uniform dull-blue fluorescence, which is greatly intensified in the presence of Zn acetate. The colour and intensity of the fluorescence may also be varied by alteration of pH, treatment with free halogens, and alteration of the wavelength of the u.v. light. By coupling with *p*-aminodiethylaniline, the salicyloylhydrazone can be converted into a brilliantly coloured blue-green indoaniline, which can be determined absorptiometrically. The estimation of ketosteroids by this method has been investigated. H. I. F.

2615. **Countercurrent distribution ("Craig" distribution).** C. Meyer (*Chem. Tech., Berlin*, 1955, **7** [5], 281–287).—A discussion is given of the principles, operation and uses of the Craig countercurrent distribution for separating or purifying substances. Various forms of the method are described in detail, and a description is given of the calculation, from the partition coefficients, of the degree of separation attainable in a given number of stages, and of the number of stages necessary to attain a desired degree of separation. A full description is given of the apparatus (and fully automatic apparatus) employed, including the

Craig drum multi-stage separator, and a number of types of separating vessel operating on the decantation principle. The Heckler separator for micro-separation is described and illustrated. Successful applications include the preparation of pure insulin from the crude product using *sec.*-butanol and 1 per cent. aq. chloroacetic acid for the partition, the detection of the various streptomycins, and the separation of a mixture of equal parts of acetic, propionic, butyric and valeric acids.

H. L. WHITEHEAD

2616. **Two-step mixed indicator for Kjeldahl nitrogen titration.** I. H. Sher (*Anal. Chem.*, 1955 **27** [5], 831–832).—A mixture of bromocresol green (**I**), New Coccine (**II**) (a dye manufactured by Ansco, Binghamton, N.Y.) and *p*-nitrophenol (**III**) is recommended as indicator for the Kjeldahl nitrogen titration. A very sharp end-point occurs, the colour changing from blue (alkaline) through grey to yellow (acid) with the addition of 0·02 ml of 0·015 *N* HCl. The grey end-point at pH 4·6 is easily seen, is sharpest by fluorescent light or daylight, and needs no standard for comparison. During an actual titration of micro-amounts of NH_3 in aq. H_3BO_3, the colours and shades change continuously below pH 7·4, and a green to blue warning occurs at about 0·5 ml of 0·015 *N* HCl before the end-point. *Preparation*—Dissolve **I** (350 mg) in 95 per cent. ethanol (10 ml), add 0·50 *N* NaOH (1·0 ml), dilute with water (200 ml), add **II** (22·1 ml of a 1 per cent. aq. soln.) and **III** (750 mg as a soln. in a few ml of ethanol) and dilute with water to 250 ml. Test a few drops in acetate or phthalate buffer of pH 4·6 and, if necessary, add small amounts of **I** or **II** to give a neutral grey colour. For high sensitivity, to this stock soln. (15 ml) add H_3BO_3 (40 g) and dilute to 2 litres with distilled water, and use 5 ml of this soln. in the usual way to trap NH_3 from the distillation; dilute to 25 ml with NH_3-free water before titration.

A. R. ROGERS

2617. **Improvement of end-point in EDTA titrations through use of manganous salts.** J. Kinnunen and B. Wennerstrand (*Chemist Analyst*, 1955, **44** [2], 33–34).—In the determination of either Cu, Ni, Co, Fe, V or Cr by titration with 0·01 or 0·02 *M* aq. EDTA (disodium salt) (**I**) (Eriochrome black T indicator) a more sharply-defined end-point can be obtained by adding either (*i*) an excess of **I** soln. and back-titrating with 0·01 or 0·02 *M* aq. $MnSO_4$ soln., or (*ii*) an excess of a 0·02 *M* soln. of the manganese salt of EDTA (prepared as described), heating to boiling point, and back-titrating the cool diluted soln. with 0·02 *M* aq. **I**. The end-points are sharper than with murexide and titrations can be effected in the presence of $NH_4^{\cdot}$. The $MnSO_4$ soln. should be standardised against the **I** soln. Detailed procedures for each of the above-mentioned elements when present alone in soln. are given. The method is also applicable to In and Al. W. J. BAKER

2618. **A study of oxidations using copper (III) reagents.** D. A. Keyworth and K. G. Stone (*Anal. Chem.*, 1955, **27** [5], 833–835).—Although 0·05 *M* soln. of potassium diperiodatocuprate^{III} and potassium ditelluratocuprate^{III} are stable and easily prepared, difficulty is experienced in end-point detection when they are used as oxidising agents in volumetric analysis; the dead-stop method appears to be the most satisfactory. The oxidation by ditelluratocuprate^{III} reagent of cyanide in 0·5 *M* KOH, or of thiosulphate in saturated $NaHCO_3$ soln., is almost quant. Applications of Cu^{III} oxidation are limited by the uncertainty of product composition and the possible competition from the oxidising action of the complexing anion.

A. R. ROGERS

2619. **Potentiometric titration using the catalytic decomposition of hydrogen peroxide on a platinum electrode.** I. E. Flis (*Zh. Anal. Khim., SSSR*, 1955, **10** [1], 38–43).—A platinum electrode immersed in a solution containing H_2O_2 changes its potential linearly with pH. The electrode can be used for the titration of acids, bases and certain salts. It is applied to the determination of active Cl, alkali and carbonate in hypochlorites and chlorites.

G. S. SMITH

2620. **Amperometric titrations with anthranilic acid.** A. K. Zhdanov, R. I. Tseĭtlin and A. M. Yakubov (*Zavod. Lab.*, 1955, **21** [1], 7–10).—Conditions for the amperometric determination of Cu, Zn, Ni and Co with 0·17 *M* Na anthranilate of pH 5·4 are studied. The optimum conditions are pH 4·5 to 5·5, 15 to 20 per cent. of ethanol, and 15 to 30 mg of the element sought in 50 ml of the solution for titration. For Cu a suitable supporting electrolyte is 0·1 or 1 *M* KNO_3 in the presence of 1 ml of 0·5 per cent. gelatin solution; the potential applied can be zero or −0·6 V. For Zn, Ni and Co the supporting electrolyte can be 0·5 to 2 *M* KNO_3, KSCN, KCl, Na_2SO_4 or Na acetate; the applied potential is −1·4 V for Zn, and −1·6 V for Ni and Co. Hydrogen is used to remove dissolved oxygen. The results for Cu, Ni, Zn and Co are satisfactory in the presence of large amounts of Mg, and salts of Mg can be used as supporting electrolytes. Aluminium (0·1 *M*) causes no interference and, with Ni and Co, Cr (0·04 *M*) causes no interference. When Pb is present the same solution can be used for an amperometric determination of Pb, using Na_2SO_4 and an amperometric determination of Cu, Zn, Ni or Co by the method described. G. S. SMITH

2621. **Densitometric titration.** S. Shinkai (*Japan Analyst*, 1953, **2** [5], 426–428).—The change in density of the supernatant liquid on a precipitation titration with a concentrated soln. ($\simeq N$) is so marked that it can be used for the indication of the end-point. Examples are given for the titration of SO_4'' with 2 *N* $BaCl_2$ and of Cl′ with *N* $AgNO_3$. When the density is plotted against the molar ratio, a distinct min. is observed at the end-point.

K. SAITO

2622. **New method of electro-analysis.** E. G. Tur'yan (*Zavod. Lab.*, 1955, **21** [1], 17–20).—The method is based on the electro-reduction of the ion or molecule under consideration at a mercury or other suitable electrode simultaneously with the separation at the platinum anode of an equivalent amount of iodine, which is titrated with thiosulphate at the end of the electrolysis, the end-point being indicated by the fall in current. The anodic yield of iodine in terms of current is 100 per cent., even at high current densities. The method is applicable when the cathode reaction takes place with 100 per cent. yield. Dissolved oxygen must be removed. A suitable apparatus for the analysis is described. The method is applied to the determination of maleic acid, nitrobenzene, 2:5-dinitrophenol, 2:4:6-trinitrophenol and 2:4-dinitro*iso*thiocyanatobenzene in *N* H_2SO_4. G. S. SMITH

2623. **The role of complex formation in partition paper chromatography.** W. F. Pickering and E. B. Jacobs (*Anal. Chim. Acta*, 1955, **12** [5], 436–442).—In the paper chromatography of various metal ions,

mixtures of ethanol with an equal vol. of 0·01, 0·001 or 0·0001 *M* disodium EDTA (**I**) are used as solvents. Variations in the concn. of **I** produce marked changes in the R_F values of the metal ions and in the spot areas, and further changes are observed when the solvent is also made 0·1 *N* in respect of H_2SO_4 or aq. NH_3. The possible mechanism of these changes is discussed and it is emphasised that conditions must be standardised when chemical reactions occur in chromatography.

W. C. JOHNSON

2624. **Charcoal chromatography with a step-graded adsorption column.** J. Porath (*Ark. Kemi*, 1955, **7** [6], 535–537).—A column is constructed of sections containing charcoal treated with stearic acid to give different degrees of saturation so that the adsorption power falls by discrete stages down the column. A substance passed through the column will move through sections of saturator concentration higher than that of the critical saturation point, but will be adsorbed in the next section, from which it can easily be eluted in good yield. It is essential that the saturator is adsorbed uniformly on the charcoal within each section, and details of a simple satisfactory procedure are given. The technique is illustrated by a description of the fractionation of pea-root exudate; the concentration of stearic acid varied from 25 per cent. in the top to 0·1 per cent. in the bottom section. The main advantage of the technique is that components of widely differing adsorbability can be separated with > 90 per cent. total yield in a single chromatogram.

A. R. ROGERS

2625. **Use of solubilising agents in gas-phase partition chromatography.** J. H. Purnell and M. S. Spencer (*Nature*, 1955, **175**, 988–989).—Column efficiency and rapidity of elution in gas-phase partition chromatography can be improved by modifying the stationary solvent to give increased solubility and greater differential elution (as shown by retention vol.). In the elution of chloromethanes with N on 38-cm columns of kieselguhr at 20° C, the use of a mixture of Teepol and water (3 + 2, by wt.) as solvent ensures a large increase in retention vol., elution occurring in order of increasing chlorine content of the mol. Since water alone is ineffective, the improvement is ascribed to enhanced solubility in the mixed solvent. Addition of 17·5 per cent. w/w of stearic acid to a 12-cm column of liquid paraffin - kieselguhr will effectively separate the chloromethanes in ≃ 15 min. by elution with nitrogen.

W. J. BAKER

2626. **The chromatography of gases and vapours. V. Partition analyses with columns of Silicone 702 and of tritolyl phosphate.** A. B. Littlewood, C. S. G. Phillips and D. T. Price (*J. Chem. Soc.*, 1955, 1480–1489).—An apparatus is described for carrying out gas partition chromatography. The vapours of various alcohols, esters and aromatic hydrocarbons are chromatographed on columns where the stationary liquid phase is either Silicone 702 fluid or tritolyl phosphate mixed with Celite. The results are given as plots of corrected retention volumes per gram of column against the reciprocal of the column temp. The data can be used to interpret and predict column behaviour, and to deduce values for the heats of soln. of the vapours in the stationary liquid phase.

J. H. WATON

2627. **Electrochromatography. VI. The change in mobility of ions and in the width of bands with change in ionic strength of the solution.** M. Maki (*Japan Analyst*, 1955, **4** [2], 74–77).—The mobilities of Ba^{++}, Hg^{++}, Fe^{+++} and Pb^{++} were measured on a filter-paper impregnated with an acetate buffer soln. containing 0 to 0·5 mole of NaCl per litre, under a p.d. of 200 V. With increase of ionic strength, the mobility of Fe^{+++} increases, that of Pb^{++} decreases, whilst that of Ba^{++} remains constant; Hg^{++} move towards the anode presumably because of the formation of an anionic complex with Cl'. When the width of the partition bands of ions is plotted against the reciprocal of the ionic strength, a straight line is obtained, which is independent of the kind of ion (Al, Ba, Ni, Co and Cu). When both the ionic strength and the pH value of the soln. with which the paper is impregnated are kept constant, the width of the band of Ba^{++} is proportional to the concn.

K. SAITO

2628. **Separation of substances by means of high-voltage paper-electrophoresis.** G. Werner and O. Westphal (*Angew. Chem.*, 1955, **67** [9–10], 251–256).—A process for paper electrophoresis is described in which high voltages of up to 10,000 V and migration passages of up to 100 cm can be used. In this process, the strip of paper is moistened with the soln. of the substances to be separated by a method which enables a long strip of paper to be moistened accurately and uniformly, and the treated paper is subjected to the charge in a "moist chamber" while lying on a synthetic-resin plate, which is cooled on the underside by a circulating cooling fluid which keeps the paper at low temp. (< 0° C). This method of indirect cooling of the paper avoids the difficulties encountered by direct cooling of the paper with cooling fluid. Condensation of moisture on to the paper in the "moist chamber" is avoided by absorption with filter-paper. A full and illustrated description is given of the use of the process for the separation of mixtures of amino acids (a mixture of glycine, alanine, α-aminobutyric acid, serine, threonine, methionine, glutamic acid, aspartic acid, hydroxyproline and dihydroxyalanine, at pH ≃ 2, temp. −7° C, 60 V per cm and 1·1 mA per cm for 200 min.), mixtures of peptides (at pH ≃ 2, 60 V per cm and 1·1 mA per cm at −11° C, for 45 and 210 min.), mixtures of sugars (glucose, mannose and rhamnose, at 50 V per cm and 1·7 mA per cm at −8° C, for 225 min.), and mixtures of inorganic ions (Fe^{++}, Co^{++}, Cd^{++}, Pb^{++}, Cu^{++} and Fe^{+++}, at pH ≃ 2, 65 V per cm and 1·15 mA per cm at −15° C, for 220 min., and colouring with H_2S or ammonium sulphide).

H. L. WHITEHEAD

2629. **A modification of Polson's simultaneous electrophoresis technique.** W. Lotmar (*Biochim. Biophys. Acta*, 1955, **16** [4], 603–604).—The use of Cellophane membranes in Tiselius cells to permit two or more simultaneous electrophoretic analyses (Polson, *Biochim. Biophys. Acta*, 1954, **13**, 451) has drawbacks due to high electrical resistance, electro-osmotic activity, impermeability to proteins and high flow resistance. In the new technique described, agar or gelatin-jelly membranes on filter-paper are used, and these difficulties are eliminated. Diagrams are given to show its application to the Kern micro-electrophoresis apparatus.

G. W. CAMBRIDGE

2630. **Ion exchangers in analytical chemistry.** O. Samuelson (*Chim. Anal.*, 1955, **37** [6], 191–198).—The use of ion exchangers in analytical chemistry is based on three different principles: the separation of exchangeable ions from non-exchangeable ions and from non-electrolytes; the separation of exchangeable ions, making use of the difference in

their exchangeabilities (ion-exchange chromatography); and the separation of non-electrolytes based on a non-ionic adsorption. Several well-established separations are quoted as examples and data are given on the separation of sugars.
J. H. WATON

2631. **Application of ion exchangers in analytical chemistry. III. The elution constants of different elements in hydrochloric acid solution.** D. Jentzsch and I. Palwik (*Z. anal. Chem.*, 1955, **146** [2], 88–102).—The examination of elements adsorbed on Wofatit L 150 described earlier (*Anal. Abstr.*, 1955, **2**, 1133) is extended to include $Bi^{\cdots}$, $Cr^{\cdots}$, Ga, $Sb^{\cdots}$ and $Zn^{\cdot\cdot}$, and a complete table of acid concentrations and elution constants is given. The factors affecting the elution constant E are discussed, with special reference to column size. The variation of E for certain metals is tabulated. Practical details for the determination of E are given. The best experimental conditions for several separations may be calculated from these results.
R. STERN

2632. **Measurement of stray light in a monochromator.** B. S. Pritchard (*J. Opt. Soc. Amer.*, 1955, **45** [5], 356–360).—In spectrophotometry the magnitude of the error due to stray light passed by the monochromator depends on the spectral distribution of the energy entering the system, the stray-light characteristics of the monochromator, the effects of any optical filters, and the spectral response of the receiver. A method is described for measuring the stray-light characteristics of a monochromator and expressing the results in a form which may be used to estimate the photometric error in any given application.
B. S. COOPER

2633. **Elimination of interferences in flame photometry.** P. Porter and G. Wyld (*Anal. Chem.*, 1955, **27** [5], 733–736).—The effects of spectra overlapping, radiation and anion interference on the flame-photometric determination of Na and K are examined, and their possible control by the use of radiation buffers, internal standards and direct injection burners is discussed. For the highest accuracy it is necessary to have considerable knowledge of the nature of the sample, and to prepare standards very similar in composition.
K. A. PROCTOR

2634. **Pressed-disc technique in infra-red spectroscopy.** V. C. Farmer (*Chem. & Ind.*, 1955, [21], 586–587).—Infra-red spectroscopy with finely ground samples dispersed in pressed discs of KBr (or other alkali halide) gives misleading results with compounds containing a hydroxyl group, owing to adsorption on the halide particles. Experiments with benzoic acid dispersed in KCl and KBr showed that this effect is minimised if the concn. of sample is not too low and if heating and prolonged grinding are avoided.
S.C.I. ABSTR.

2635. **Principles of precision colorimetry. A general approach to photo-electric spectrophotometry.** C. N. Reilley and C. M. Crawford (*Anal. Chem.*, 1955, **27** [5], 716–725).—Variations in slit width, sensitivity and dark-current setting have been shown to affect spectrophotometric precision unless the limiting precision of reading the dial is due to light-source fluctuations. Four spectrophotometric procedures are examined. Two of these are new and may offer a possible increase in precision, but require more time and effort than normal methods.
K. A. PROCTOR

2636. **Gas analysis by thermal-conductivity measurements.** G. B. Brown and R. W. Dean (*Instrum. Engr.*, 1955, **1** [7], 145–150).—The thermal-conductivity method of gas analysis is restricted to the quant. analysis of mixtures of known constituents and of a known range of composition. For gases other than binary mixtures, the measured constituent must have a thermal conductivity markedly different from that of the other constituents, or these other constituents must have equal conductivities, be present in fixed proportions or vary with the measured constituent in a fixed and definite manner. Despite its limitations the method is used in connection with a number of industrial processes. Various types of equipment are described, together with applications of the thermal-conductivity method in flue-gas analysis (continuous measurement of the CO_2 content), sulphuric acid manufacture, and the production of NH_3 by the Haber process, etc.
J. M. JACOBS

2637. **Gas micro-analysis (absorption and explosion methods).** A. Mizuike (*Japan Analyst*, 1954, **3** [1], 17–21).—Quantitative analysis of a very small amount of gas (10^{-3} to 10^{-4} ml) was studied with a view to improving the apparatus. Anhydrous glycerol was used for the confining liquid and the small bubble was treated successively with various gas absorbers, the decrease in volume being measured under a microscope. The explosion method can also be used on a micro scale. Attempts were made to keep the shape of the bubble similar. Physical dissolution of gas in the confining liquid or in the absorbents appears to be a big source of error.
K. SAITO

2638. **The analyst in the fine chemicals and pharmaceutical industries.** G. E. Foster (*Chem. & Ind.*, 1955, [27], 754–759).—This lecture deals with the methods of sampling and analysis used in a modern control laboratory of a firm of manufacturing pharmaceutical chemists.
N. E.

2.—INORGANIC ANALYSIS

2639. **Detection and separation of metal ions on paper impregnated with 4-hydroxybenzothiazole.** Q. Fernando (*Anal. Chim. Acta*, 1955, **12** [5], 432–435).—Paper strips impregnated with 4-hydroxybenzothiazole are used for the chromatographic detection and separation of various metal ions. Methanol and ethanol are used as solvents in the descending technique. The chromatograms are exposed to NH_3 vapour and are examined in daylight and in u.v. light. The following fluorescence effects are observed: $Zn^{\cdot\cdot}$, $Mg^{\cdot\cdot}$ and $Cd^{\cdot\cdot}$, intense blue; $Ag^{\cdot}$, blue-green; $ZrO^{\cdot\cdot}$, greenish yellow; $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$ and $Ba^{\cdot\cdot}$, pale blue; $Li^{\cdot}$, $Na^{\cdot}$, $K^{\cdot}$ and $Rb^{\cdot}$, very pale blue. 4-Hydroxybenzothiazole forms no fluorescent compounds with $Al^{\cdots}$ and $Be^{\cdot\cdot}$ (a distinction from 8-hydroxyquinoline). The fluorescence due to $Zn^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Mg^{\cdot\cdot}$ and $Ag^{\cdot}$ persists for 3 min. on exposure of the moistened spots to acetic acid vapour, but the fluorescence due to $Li^{\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, $Rb^{\cdot}$, $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$ and $Ba^{\cdot\cdot}$ is quenched in 10 to 15 sec. The reaction detects 0·25 μg of $Zn^{\cdot\cdot}$, 0·1 μg of $Cd^{\cdot\cdot}$ and 1 μg of $Mg^{\cdot\cdot}$, but is masked by $Fe^{\cdots}$, which forms a bluish-green complex. R_F values obtained with methanol and ethanol, respectively, are: $Fe^{\cdots}$, 0·59, 0·57; $Al^{\cdots}$, 0·65, 0·66; $Zn^{\cdot\cdot}$, 0·10, 0·15; $Cd^{\cdot\cdot}$, 0·22, 0·23; $Cu^{\cdot\cdot}$, 0·25, 0·21; $Ni^{\cdot\cdot}$, 0·15, 0·16; $Co^{\cdot\cdot}$, 0·25, 0·20.
W. C. JOHNSON

2640. **Micro-determination of metals by electrolysis without applied voltage.** A. Okáč and L. Sommer (*Chem. Listy*, 1954, **48** [8], 1137–1150).—Conditions for the determination of small amounts of Bi, Sb and Cu, alone and in the presence of Pb, Ni, Co and Fe, by electrolysis without applied voltage, have been studied. The analyses are carried out in a special, simply constructed apparatus (illustrated), consisting of platinum gauze as the cathode and a rod of spectrally pure lead or aluminium, coated with a film of collodion, as the anode. The method, accurate within ± 1 per cent., is suitable for determining Cu in ordinary steel, but fails with alloy steel. *Determination of bismuth*—The soln. containing 1 to 5 mg of Bi in 50 to 60 ml is treated with 20 per cent. HNO_3 and electrolysed (lead anode) for 30 min. at 90° C, the initial current being 25 to 30 mA and the residual current 12 to 20 mA. In the presence of much Pb, *M* tartaric acid (5 ml) and urea (2 g) are added to the sample (50 to 60 ml) containing 20 per cent. HNO_3 (3 to 5 ml) before electrolysis. *Determination of antimony*—A mixture of the soln. (1 to 5 mg of Sb in 50 to 60 ml), 20 per cent. HNO_3 (2 to 7 ml), *M* tartaric acid (2 to 5 ml), hydroxylamine hydrochloride (10 g) and urea (2 g) is electrolysed (lead anode, initial current 12 to 15 mA) at 85° to 90° C for 40 min. *Determination of copper*—To the sample containing 1 to 5 mg of Cu are added urea (8 to 10 g), 20 per cent. HNO_3 (2 to 4 ml) and *M* tartaric acid (5 ml), to a total volume of 50 to 60 ml of pH 1 to 2. The soln. is electrolysed (lead anode, initial current 12 to 14 mA) for 40 min. at 85° to 90° C. In the presence of a large excess of Pb, the amount of urea added is 10 to 12 g, the temp. 72° to 82° C and the current 10 to 20 mA. Similar conditions are used to determine Cu in the presence of Ni. If Bi is present, Cu is determined by adding 20 per cent. HNO_3 (3 to 4 ml), 0·1 *M* EDTA (disodium salt) (10 ml) and urea (8 to 10 g) to a 40-ml sample, and electrolysing at 90° C for 40 min. More accurate results are obtained by using an aluminium electrode activated with hot 25 per cent. KOH. In one procedure, the sample (1 to 6 mg of Cu in 40 ml) is treated with 4 *N* H_2SO_4 (1 ml), 10 per cent. HCl (0·5 ml), *M* hydroxylamine hydrochloride (5 ml) and *M* tartaric acid (5 ml), and electrolysed for 35 to 40 min. at 90° C with an initial current of 12 mA. In another procedure, the hydroxylamine and tartaric acid are replaced by 3 to 5 g of NaH_2PO_2. Copper in the presence of $Fe^{\cdots}$ is determined similarly. A procedure for the determination of Cu in ordinary steel is given. G. Glaser

2641. **Determination of small amounts of nitrogen and oxygen impurities in hydrogen and helium.** K. N. Zinov'eva (*Zavod. Lab.*, 1955, **21** [1], 30–32).—A method based on the absorption of nitrogen and oxygen on charcoal at the temp. of liquid nitrogen is described. G. S. Smith

2642. **Reagent for the quantitative determination of very small amounts of water in gases, liquids and solid substances, and method of preparing the reagent.** J. H. van der Meulen (Brit. Pat. 728,947, Date Appl. 13.4.53).—The Karl Fischer reagent for moisture determination has disadvantages in that pyridine of high purity is required, and also in that the pyridine may form further compounds with components in the reaction mixture. Reagents are suggested in which the H_2SO_4 and HI liberated in the moisture determination are bound by alcoholates, phenoxides, acetates or other salts of weak organic acids, suitably chosen to prevent insoluble substances from forming and side reactions from occurring. A mixture of sodium and zinc acetates gives very good results and is easy to dissolve. One example of a reagent is prepared as follows. A mixture of 25 g of NaI, 85 g of dry sodium acetate and 63·5 g of I is dissolved in 600 ml of pure methanol. A 4 *M* soln. (90 ml) of SO_2 in methanol is added and the soln. is made up to 1 litre with methanol. The 85 g of dry sodium acetate may be replaced by 41 g of sodium acetate and 46 g of zinc acetate. J. H. Waton

2643. **Volumetric determination of water. Karl Fischer titration. I. Effect of temperature on the titration.** V. G. Jensen (*Dansk. Tidsskr. Farm.*, 1955, **29** [4], 77–88).—For the purpose of correcting for differences between the temp. at which the reagent is used and the temp. at which it has been standardised, the value 0·0012 per °C may be taken as the coeff. of expansion of the reagent. P. S. Arup

2644. **The spectrochemical determination of argon in air.** T. Lee (*Applied Spectroscopy*, 1955, **9** [1], 5–13).—A method is described in which the direct-reading spectrograph (*Anal. Abstr.*, 1955, **2**, 1997) is used for the measurement of the argon content of air samples containing slightly more or less than that of the normal atmosphere. The sample is fed into a discharge tube and excited by external electrodes connected to a 150-Mc.p.s. generator. Absolute intensity measurements on the argon line 4158·6 A are corrected for background, but no advantage was found in using the nitrogen band-head at 3998·4 A as internal standard. The precision is ± 0·43 per cent. at the 95 per cent. confidence level on a single determination, which can be made in 1 min. P. T. Beale

2645. **Quantitative spectrochemical analysis by flame photometry. I. Determination of alkali metals by flame photometry.** R. Ishida (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [1], 56–60).—The influence of the stability of the light source of flame spectra was compared with that of arc spectra. The effect due to different intensities of the background can be eliminated by the use of an internal standard element (*e.g.*, Rb for K). The interference of "Swan" bands is negligible when a constant-deviation prism is used. The mutual influence of alkali metals and alkaline-earth metals was also studied; the use of an internal standard (most preferably an alkali metal which is absent in the sample soln.) is again advantageous to eliminate the effect. Examples of the analysis of silicate rocks are given. K. Saito

2646. **Quantitative spectrochemical analysis by flame photometry. II. Determination of lanthanum by the use of band spectra of lanthanum oxide.** R. Ishida (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [1], 60–63).—An aqueous soln. containing La is burnt in an acetylene - air flame and the emission spectra are observed photographically. The intensity of the band spectra of LaO at 560 mμ and 440 mμ was measured on the plate to give standard curves that are linear within the range 0·003 to 0·03 per cent. of La. The band spectrum at 790 mμ can also be used for quant. analysis when the intensity is measured directly with the Perkin - Elmer photometer. No interference results from the presence of other rare-earth elements provided that their total amount is less than that of La. When Al, $Fe^{\cdots}$, Na, K and NH_4^+ are present in the soln., a significant interference results. Silicate samples

(minerals, glasses, etc.) are decomposed and rare-earth elements are separated by the pptn. of the oxalates, which are weighed, dissolved in an acid and submitted to flame photometry. K. SAITO

2647. **Mutual separation of alkali metals with ion-exchange resin.** H. Okuno, M. Honda and T. Ishimori (*Japan Analyst*, 1953, **2** [5], 428–432).—The ion-exchange equilibrium constant K_H^M (M = Li, Na or K) between alkali-chloride soln. (0·1 *N*) and Amberlite IR-120 (H) increases with the alcohol content of the soln. (up to 50 per cent. by vol.), to an extent that decreases in the order Li, Na, K. By means of a mixture (7 + 3) of HCl (0·2 *N*) and methanol, lithium ions are eluted practically free from Na^+ and K^+ from a column (exchange capacity 25 milli-equiv.) containing up to 5 milli-equiv. of alkali ions. Sodium and potassium ions are subsequently eluted, almost free from each other, with 0·2 *N* and 0·5 *N* HCl successively. This method can be applied to the purification of Li. K. SAITO

2648. **Iodimetric determination of copper in nitric acid medium.** N. I. Matveev and N. E. Kazakevich (*Zavod. Lab.*, 1955, **21** [4], 405–406).—Published methods for economising on KI used in the iodimetric method for determining Cu and for improving the accuracy of the titration are discussed and the following variant is recommended. *Procedure*—The material (0·5 to 1 g) is heated with 25 to 30 ml of aqua regia to complete decomposition, the solution is evaporated nearly to dryness and then taken to fuming with 20 ml of dil. H_2SO_4 (1 + 1). The cooled residue is mixed with 50 to 70 ml of water and the solution, after being heated, is filtered into a conical flask and diluted to about 200 ml. The hot solution is treated with warm 20 per cent. $Na_2S_2O_3$ solution and boiled to coagulate the copper sulphide and sulphur. The ppt. is filtered off and washed with hot water, ignited at 500° to 600° C and dissolved in 3 to 4 ml of dil. HNO_3 (1 + 1). The solution is evaporated in the crucible to 1 to 2 ml, transferred to a conical flask with 20 ml of water, cooled, treated with 5 ml of HNO_3 (free from oxides of N), 5 ml of urea solution (200 g of urea, 3 g of lead acetate and a small amount of HNO_3 in 1 litre of water) and 5 ml of iodide mixture (12 g of KI, 40 g of KBr and 70 g of potassium or ammonium thiocyanate in 1 litre of water), and titrated with thiosulphate solution (7·5 g of $Na_2S_2O_3$, 10 mg of Na_2CO_3 and 0·4 ml of $CHCl_3$ in 1 litre), starch solution being added towards the end of the titration. G. S. SMITH

2649. **A rapid method for the determination of copper in mineral oils.** C. E. S. Hackett (*Anal. Chim. Acta*, 1955, **12** [4], 358–362).—In the determination of Cu in mineral oils, preliminary combustion or oxidation of the sample causes large errors. Greater precision is attained by direct extraction, and the following method is suitable for the determination of 10 to 100 μg of Cu. *Procedure*—Weigh 10 to 100 g of the oil into a separating funnel and dilute with an equal vol. of petroleum spirit (B.S. 148: 1951, App. B). Extract the oil twice with 10-ml portions of a mixture of 1 vol. of conc. HCl with 10 vol. of industrial alcohol, and finally with 10 ml of industrial alcohol. To the combined extracts add 10 ml of a soln. of 30 g of anhyd. Na acetate in 100 ml of water, and 10 ml of aq. 10 per cent. $NH_2OH.HCl$; mix and add 5 ml of a 0·1 per cent. soln. of 2:2′-diquinolyl (cuproine) in industrial alcohol. Extract first with 10 ml then with 5 ml of $CHCl_3$, dilute the combined extracts to 50 ml with industrial alcohol and determine the absorption on a Spekker absorptiometer with a 4-cm cell, Ilford Spectrum yellow green No. 605 filter and a water setting of 1·0. Determine, and apply, a correction for the reagent blank. Prepare a calibration curve with measured quantities of standard Cu^{++} soln. (1 ml ≡ 10 μg of Cu^{++}) mixed with 20 ml of HCl - alcohol mixture and treated as for the acid extract. W. C. JOHNSON

2650. **Amperometric determination of copper and nickel in alloy steel by means of rubeanic acid.** Kh. Ya. Levitman and Z. A. Krivchik (*Zavod. Lab.*, 1955, **21** [4], 397–399).—Amperometric titration at 1·3 V of a mixture of copper and nickel salts in ammoniacal medium with rubeanic acid gives a graph showing lines of different slopes corresponding to the different solubilities of the copper and nickel rubeanates, and permits the content of each to be determined. *Procedure*—Treat a 0·5-g sample of steel with 25 ml of dil. (1 + 1) HCl, add conc. HNO_3, dropwise, to complete dissolution of the metal, evaporate the solution to dryness in a porcelain dish, and dissolve the residue in 4 ml of dil. (1 + 1) HCl and 3 ml of water. Cool the solution, transfer to a 100-ml calibrated flask, add 15 ml of aq. NH_3 soln. (25 per cent.) and 10 ml of 0·5 per cent. gelatin soln., make up to the mark and shake. Transfer a suitable volume of the clear solution after settling of the ppt. to an electrolysis cell, and titrate with a standard solution of rubeanic acid in ethanol. The titre of the acid is found by titrating a standard nickel solution in 0·5 *M* aq. NH_3 or by titrating a second aliquot portion of the test solution after adding a known amount of nickel solution. G. S. SMITH

2651. **Thermal and thermogravimetric analysis of hydrated cupric chloride.** J. Kamecki and J. Trau (*Bull. Acad. Polon. Sci., III*, 1955, **3** [2], 111–115).—To investigate conflicting views on the hydrates of cupric chloride and establish temp. of decomposition, a series of thermal and thermogravimetric analyses were carried out. Thermal analyses were made in the following temp. ranges: 68° to 200° C, 2° to 210°C or 20° to 230°C, with a Ni - Ni/Cr thermocouple and self-registering potentiometer. Cold ends of the thermocouple were placed in a Dewar flask filled with water at 20° C. Samples of the powdered salt (≃ 4 g) were placed in a glass test-tube within a cylindrical block of copper and heated in a furnace. Heating curves were ascertained and defined by comparison with the "furnace curve" (curve for neutral substance, NaCl, under the same conditions). The rate of heating was 2·22° C or 3·02° C per min., and results were confirmed by differential thermal analysis. From the thermal analysis curves it was concluded that, in the temp. range 2° to 131° C, only one hydrate of cupric chloride exists, of composition $CuCl_2.2H_2O$, which at 131·8° C loses completely both molecules of water. R. J. MAGEE.

2652. **Micro-determination of silver and gold by electrolysis without applied voltage.** L. Sommer (*Chem. Listy*, 1954, **48** [8], 1151–1155).—Electrolysis without applied voltage can be used for the determination of trace amounts of Ag and Au, using lead or copper anodes coated with collodion. *Determination of silver*—By using a lead anode and an initial current of 8 mA, a soln. prepared by mixing the sample (1 to 5 mg of Ag in 40 ml) with 20 per cent. HNO_3 (3 to 5 ml) and *M* tartaric acid (10 ml)

is electrolysed at 90° to 92° C for 30 min. An excess of Pb as large as 3000-fold may be present. By using a copper anode, Ag is determined under similar conditions except for the addition of tartaric acid. The deposition of the metal is accelerated and the adherence of the deposit improved by the addition of 0·1 *M* EDTA (disodium salt). In the presence of Cu^{++} (up to a 300-fold excess) the following procedure must be applied. The hot soln. of Ag^{+} and Cu^{++} (50 ml) is treated with 20 per cent. HNO_3 (1 to 2 ml) and, after electrolysing for 15 min., with urea (5 g); the total time of electrolysis is 35 min., temp. 90° C and current 8 mA. A procedure for the determination of Ag in galena, in which the ore is first decomposed by oxidation with HNO_3 and H_2O_2, is given. *Determination of gold*—To a 50-ml soln. of Au^{+++} is added 20 per cent. HNO_3 (1 ml) and 10 per cent. HCl (0·2 ml), and the soln. is electrolysed (Cu anode, initial current 8 mA) for 30 to 40 min. at 85° to 87° C. Separation of Au from Ag is not possible. G. GLASER

2653. **Beryllium—its estimation and separation from aluminium.** C. L. Sastri, G. Sriramulu and B. S. V. Raghava Rao (*J. Sci. Ind. Res., B, India*, 1955, **14** [4], 171–174).—Determinations of beryllium were carried out with oxine, benzylamine and triethanolamine. The oxine ppt. was determined by (1) drying the well-washed ppt. for 6 to 8 hr. at 80° C, and (2) bromination. Benzylamine and triethanolamine ppt. Be as hydroxide. The separation of Be from Al was investigated by the use of *p*-chloroaniline and acridine; both ppt. Al completely, leaving Be in solution. When the amount of Al is small, satisfactory separation is obtained with triethanolamine. G. C. JONES

2654. **Chemical analysis of beryllium. X. Separation of beryllium with hydrogen sulphide accompanied by extraction of iron with ether.** T. Akiyama (*Japan Analyst*, 1954, **3** [1], 33–34).—An experiment similar to that described in Part VIII (*cf. Anal. Abstr.*, 1955, **2**, 2353) was carried out in the presence of a large amount of Fe. To avoid the adsorption of Be by FeS, most of the Fe was removed by ether extraction. The separation of Al and Be in the filtrate from the pptn. of sulphides of Ni, Co, etc., was achieved by the oxine method. **XI. Determination of beryllium with selenous acid.** (*Ibid.*, 1954, **3** [1], 35–37).—Kota's method (*Chem. Zbl.*, 1933, **104** [11], 254) was re-examined. For a soln. containing only Be this method provides better results than the ordinary ammonia method. Separation from Cu, Mn, Bi, Ti and Hg is satisfactory when the ppt. is obtained at pH 4·2 to 5·5. **XII. Determination of beryllium as sulphate.** (*Ibid.*, 1954, **3** [2], 127–129).—Cupr's method (*Z. anal. Chem.*, 1929, **76**, 173) was examined and it was found that the average deviation from the mean is $\simeq$ 0·3 per cent. Iron and Al are removed as mentioned in the earlier parts of this investigation (see above, Part X). **XIII. Separation of aluminium and beryllium with hydrochloric acid and ether.** (*Ibid.*, 1954, **3** [2], 129–131).—Haven (*Amer. J. Sci.*, 1897, **4**, 111) and Machatschki's (*Z. Kristallogr.*, 1926, **63**, 457) method of separating Be from Al, utilising different solubilities of their chlorides in ether saturated with HCl, was re-examined. When a large amount of Fe is present, it must be removed as FeS subsequent to the pptn. of $AlCl_3.6H_2O$ with ether. **XIV. Determination of beryllium with organic amines.** (*Ibid.*, 1954, **3** [5], 410–412).—The use of ethylamine and methylamine carbonates and hydrazine carbonate in place of aq. NH_3 soln. was studied. When Be is pptd. with these organic amine carbonates at pH 6 to 7, bromothymol blue being used as indicator, a stable basic carbonate is obtained, which is easily filtered off and ignited to BeO. Ammonium phosphate as the pptg. reagent was found to be no better than aq. NH_3 soln. K. SAITO

2655. **Colorimetric determination of sub-microgram quantities of magnesium.** V. A. Nazarenko and E. A. Biryuk (*Zavod. Lab.*, 1955, **21** [1], 20–22).—The formation of a pink colour with Eriochrome blue - black B can be used to detect 0·01 to 0·02 μg of Mg in 2 ml of soln. To determine 0·05 to 0·30 μg of Mg, 2 ml of the solution in a small separating funnel are mixed with 0·20 ml of 0·5 per cent. Na diethyldithiocarbamate (**I**) soln. and the mixture is shaken with 1 ml of ethyl acetate. The ethyl acetate layer is rejected and the operation of adding **I** and extracting is repeated several times, until the ethyl acetate no longer shows the yellow colour due to the presence of Fe. The aq. solution is then evaporated to dryness, the residue is dissolved in 3 ml of water, and 0·20 ml of 0·02 per cent. of the Eriochrome blue - black B in ethanol, together with 0·20 ml of 10 per cent. aq. NH_3 solution, are added, and the extinction of the solution is measured at 660 mμ in a 10-mm cell. The concn. of Mg is determined from a calibration curve. G. S. SMITH

2656. **Colorimetric determination of magnesium in cast or pig iron.** N. Yokouchi (*Japan Analyst*, 1954, **3** [1], 3–7).—Magnesium (0·01 to 0·2 per cent.) in cast or pig iron (sample $\simeq$ 0·3 g) is separated from Fe by the pptn. of $Mg(OH)_2$ in the presence of KCN. The ppt. is dissolved in HCl, and small amounts of Fe, Mn and Ca are pptd. with aq. NH_3 soln., $KMnO_4$ and NH_4 oxalate, respectively. Magnesium is pptd. as oxinate in a basic soln., then dissolved in HCl and treated with sulphanilic acid and $NaNO_2$ to give an orange colour. The colour remains unchanged for 2 hr. and is in accord with Beer's law for $<$ 0·4 mg of Mg per 100 ml. The amount of sulphanilic acid and $NaNO_2$ (0·3 per cent., 1·0 to 2·0 ml for each) should be kept approx. constant for a reproducible result to be obtained. K. SAITO

2657. **Determination of magnesium in the presence of calcium by titration with 8-hydroxyquinoline.** M. Kobrová (*Chem. Listy*, 1954, **48** [8], 1167–1170).—In a new volumetric method for the determination of Mg, unaffected by the presence of even relatively large amounts of Ca, a standard soln. of 8-hydroxyquinoline acetate (**I**) is used, with Eriochrome black T as indicator. It has been applied to the determination of Mg in mineral waters. *Procedure*—The sample of mineral water (100 g) is treated with 2 *N* NH_4Cl (20 ml), a buffer soln. [NH_4Cl (54 g) and 35 per cent. aq. NH_3 (250 ml) in 1 litre of water] (10 ml) and with the indicator to give a clear wine-red colour, and titrated hot with 0·1 *N* **I**. The end-point is marked by a colour change from red to blue; this colour should persist when the soln. is boiled and treated with an additional 5 ml of the buffer. To determine Mg in mineral waters with a high content of Mg, a sample (10 g) is diluted to 400 ml, 2 *N* NH_4Cl (40 ml) and the buffer (15 ml) are added, and the procedure is continued as above. The addition of more indicator during the titration is recommended. G. GLASER

2658. **Compleximetric determination of calcium [in fluorspar].** W. Nielsch (*Glas-Email-Keramo-Tech.*, 1955, **6** [3], 75–78).—This titrimetric method depends on the fact that the complex of $Ca^{\cdot\cdot}$ with EDTA (disodium salt) does not, with ammonium purpurate (murexide), give the intense salmon-red colour given by the free ion. Interference by Mg and the heavy metals (Ag, Cu, Cd, Hg, Co, Ni, etc.) is prevented by the addition of triethanolamine and of KCN, respectively. A 1-g sample of fluorspar is heated to dryness with 5 ml of conc. H_2SO_4 and the solid is boiled (1 to 3 hr.) with 400 ml of a solution which contains 20 ml of conc. H_2SO_4 + 100 ml of conc. HCl per litre. The clear filtrate is made up to 500 ml. To 50 or 100 ml of this solution are added 30 ml of a 30 per cent. solution of triethanolamine and a few crystals of KCN, and the pH is adjusted to $\not<$ 12 by the addition of, *e.g.*, 25 ml of a 10 per cent. solution of NaOH. A mixture (0·2 g) (freshly mixed and ground) of 1 g of murexide and 100 g of NaCl is added and the solution is titrated with a standard solution of EDTA (disodium salt) (93·05 g per 5 litres) to the colour change from red to blue. If x ml is the titre for 100 ml of the sample solution, the fluorspar sample contains $x \times 1{\cdot}9520$ per cent. of CaF_2. The method is rapid and the results agree with those of the classical pptn. as Ca oxalate. J. A. SUGDEN

2659. **Examination of the interference of phosphate ion in the titrimetric determination of calcium and magnesium with EDTA.** R. E. Collier (*Chem. & Ind.*, 1955, [21], 587–588).—On the assumption that interference by PO_4''' is due to the fact that the ion product exceeds the solubility product of calcium diphosphate, a series of photometric titrations was carried out in order to determine ratios of P:Ca below which there is no interference. Difficulty was experienced in establishing clear-cut values at which interference began, since its onset appears to be gradual. An arbitrary criterion was therefore adopted whereby titrations completed within 4 min. were taken as satisfactory and the remainder regarded as vitiated by interference. With only 0·1 mg of Ca in 70 ml, a 30:1 ratio of P:Ca caused no appreciable interference with the murexide titration, whilst the Solochrome black T titration is even less affected by the PO_4'''. There is an approx. inverse relation between content of Ca and max. permissible content of PO_4'''. With determinations of Mg, interference with the Solochrome black T titration is more serious, but it was found that 1 mg of Mg in 70 ml can be titrated accurately in the presence of 1 mg of P provided that the titration is completed immediately after the addition of the ammonia buffer. S.C.I. ABSTR.

2660. **Flame-photometric micro-method for the determination of calcium, strontium and barium present together.** A. Hegedüs, T. Millner and E. Pungor (*Magyar Kém. Foly.*, 1953, **59** [10], 304–309; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 610).—A Beckman DU spectrophotometer with a hydrogen - oxygen flame is used for the determination of Ca, Ba and Sr, when the three metals are present together. The optimum pressure of hydrogen is 0·14 atm., and of oxygen 1·09 atm. For 0 to 800 μg per ml of test element and 0 to 1200 μg per ml of the other elements, the interference is insignificant under the following conditions: Ca at 424 mμ, slit-width 0·1 mm; Sr at 460 mμ, slit-width 0·1 mm; Ba at 870 mμ, slit-width 0·2 mm. The error is $\pm$ 2 per cent. E. HAYES

2661. **EDTA titrations using Zincon as indicator.** J. Kinnunen and B. Merikanto (*Chemist Analyst*, 1955, **44** [2], 50).—Zincon (2-carboxy-2′-hydroxy-5′-sulphoformazylbenzene) can effectively replace Eriochrome black T as internal indicator for titrations with ethylenediaminetetra-acetic acid (**I**). The indicator is prepared by dissolving finely powdered Zincon (0·13 g) in aq. *N* NaOH and diluting to 100 ml with water. With this indicator, only Zn can be titrated directly with **I** in a buffered ammoniacal soln. (pH 9 to 10); for Cu, Ni, Co, Mn, $Fe^{\cdot\cdot\cdot}$, Cd, Pb, $Ce^{\cdot\cdot\cdot}$, In and Ca, an excess of **I** is added and the excess is then titrated with standard zinc soln. When determining Al or Cr, **I** is added to a slightly acid soln., which should be boiled before aq. NH_3 is added. W. J. BAKER

2662. **Detection of zinc in copper sulphate.** M. Langejan and J. A. C. van Pinxteren (*Pharm. Weekbl.*, 1955, **90** [10], 333–336).—For the determination of small amounts of Zn in $CuSO_4$, separation by the H_2S method is unsatisfactory owing to co-pptn., and separation by the NaOH method (with an excess of NaOH) is only moderately satisfactory. Max. sensitivity is achieved by first removing the bulk of the Cu, and then applying the $Hg^{\cdot\cdot}$ - NH_4SCN reaction (*cf.* B.P. 1953) which gives characteristic colour reactions for various amounts of Zn in the presence of the remaining traces of Cu. *Procedure*—To 1 ml of a 10 per cent. soln. of the sample are added 0·25 ml of dil. HCl and $\simeq$ 0·3 g of aluminium foil; after being heated during 5 min. in boiling water, the clear liquid is decanted and heated with 1 drop of 3 per cent. H_2O_2 in order to oxidise traces of $Fe^{\cdot\cdot}$ to $Fe^{\cdot\cdot\cdot}$. The cooled soln. is mixed with 3 drops of an aq. soln. containing 8 g of $HgCl_2$ and 9 g of NH_4SCN per 100 ml, and (for the removal of $Fe^{\cdot\cdot\cdot}$) 1 drop of H_3PO_4; in the absence of Zn, the crystals that form on scratching the sides of the tube are green, in the presence of 0·1 per cent. of Zn, faintly violet, and in the presence of increasing amounts of Zn, violet - black shading into violet. P. S. ARUP

2663. **Determination of free cyanide and zinc in zinc cyanide solutions.** R. F. Muraca (*Plating*, 1954, **41**, 1018–1025).—Free cyanide in electroplating soln. is generally defined as the NaCN in excess of the amount required (*a*) to keep all metal compounds in soln. or (*b*) to form a metal complex cyanide corresponding to a definite formula, *e.g.*, $Na_2Zn(CN)_4$. The objections to these definitions are critically discussed, and a new definition is proposed, namely the activity of the CN′ expressed as NaCN in the bath at operating conditions. Liebig's argentimetric titration method of CN′ determination and Denigès's modification for the end-point detection with KI in an ammoniacal medium are considered with respect to their potentiometric titration curves. It is shown that potentiometric titration of 0·03 *M* $Zn(CN)_2$ soln. in 0·1 *M* $NaAg(CN)_2$ at pH 10, 8 and 12 yields results for CN′ in excess of $Na_2Zn(CN)_4$, CN′ in excess of $Zn(CN)_2$, and total CN′, respectively. An analytical procedure for zinc cyanide plating soln., based on these findings, is presented. METALL. ABSTR.

2664. **Determination of trace amounts of zinc in metallic cadmium.** G. Scacciati and A. D'Este (*Chim. e Ind.*, 1955, **37** [4], 270–272).—The determination of zinc present as an impurity in cadmium is carried out by a rapid method involving

treatment with metallic Hg to give an amalgam containing $\not>$ 5 per cent. of Cd, followed by partial anode dissolution of the amalgam. The dissolution is carried out in 0·10 *N* H_2SO_4 at 0·10 to 0·15 V and 0·007 to 0·01 amp., so that all the Zn and only a small amount of Cd is dissolved, the amount of Cd being too small to affect the polarographic or gravimetric determination of Zn. Full analytical details are given, and the theory, control and results of the method are discussed. An accuracy of $\simeq \pm 5$ per cent. is attained. C. A. FINCH

2665. **The determination of cadmium with dithizone in the presence of small quantities of nickel and cobalt.** A. Petzold and I. Lange (*Z. anal. Chem.*, 1955, **146** [1], 1–4).—To an alkaline solution of the metals add conc. dimethylglyoxime in 2 per cent. NaOH solution. The Ni forms the familiar red ppt. and Co gives a soluble yellowish-brown complex. In this form neither metal reacts with dithizone and they remain in the alkaline aqueous layer on extraction with CCl_4. Tables of determinations of Cd in the presence of Co and Ni, singly and together, are given. The results obtained in the presence of Ni are not quite as good as those obtained in the presence of Co. The removal of Zn, Cu, Hg, Pb, Sn, Bi and Ag is carried out first by the method of Fischer and Leopoldi (*Mikrochim. Acta*, 1937, **1**, 30). R. STERN

2666. **Derivatives of anthrarufin, chrysazin and quinizarin [1:5-, 1:8- and 1:4-dihydroxyanthraquinones] as colorimetric reagents for boron.** E. C. Cogbill and J. H. Yoe (*Anal. Chim. Acta*, 1955, **12** [5], 455–463).—When quinalizarin (1:2:5:8-tetrahydroxyanthraquinone) is used as a reagent for B, the colour produced has an absorption max. at 605 mμ, whereas the uncombined reagent has a max. at 575 mμ and, at 605 mμ, has an absorption 65 per cent. of that of the B compound. This overlapping is far less marked with certain derivatives of other hydroxyanthraquinones. Of these derivatives, dinitrochrysazin (4:5-dihydroxy-1:8-dinitroanthraquinone) is less sensitive (1 in 15×10^6) to B than quinalizarin (1 in 35×10^6); the others show the following sensitivities: diaminoanthrarufin (4:8-diamino-1:5-dihydroxyanthraquinone), 1 in 40×10^6; diaminochrysazin (4:5-diamino-1:8-dihydroxyanthraquinone), 1 in 50×10^6; dinitroanthrarufin (4:8-dihydroxy-1:5-dinitroanthraquinone), 1 in 45×10^6; tribromoanthrarufin [1:5:(?)-tribromo-4:8-dihydroxyanthraquinone], 1 in 100×10^6; dicyanoquinizarin (2:3-dicyano-1:4-dihydroxyanthraquinone), 1 in 100×10^6. Each substance is used as a soln. in conc. H_2SO_4, which is mixed with the borate soln., also in conc. H_2SO_4. The colour reaches a max. in $\not>$ 1 hr. Beer's law is followed approx. up to a boron concn. of 0·4 p.p.m. W. C. JOHNSON

2667. **Estimation of boron in steel.** L. Lenard and C. Dussart (*Chim. Anal.*, 1955, **37** [6], 207–211).—The colorimetric methods for the determination of boron in steel with quinalizarin, as described by Rudolph and Flickinger (*Steel*, 1943, **112**, 114) and by Weinberg, Proctor and Milner (*Ind. Eng. Chem., Anal.*, 1945, **17**, 419), are discussed. Suggestions are made for eliminating errors due to the presence of boron in the reagents and apparatus, or errors inherent in the method. Details of the procedure are given. J. H. WATON

2668. **Photometric determination of aluminium in steel.** K. Wacykiewicz (*Prace Inst. Minist. Hutnic.*, 1955, **7** [1], 35–42).—Small amounts (up to 0·05 per cent.) of Al in steel were determined photometrically with: (*a*) aluminon (ammonium aurinetricarboxylate), prepared three days before use and buffered to pH 5·3; (*b*) with Eriochrome cyanine (a red - violet dye), after elimination of Fe by mercury-cathode electrolysis and subsequent pptn. with NaOH, and adjustment of the medium with an acetate buffer of pH 6·3. The Eriochrome cyanine method was found to be simpler and more convenient. Results obtained by a Pulfrich photometer (with a filter of max. transparency at 530 mμ) had an accuracy of $\pm$ 0·002 per cent. of Al. They could be improved by applying monochromatic light. *Procedure*—A solution of 1 g of sample in 20 ml of H_2SO_4 (1:9) and 5 ml of HNO_3 (1:1) was evaporated to dryness, dissolved and boiled with 80 ml of H_2O, filtered and washed with hot water. The ppt., fused with 0·5 g of K_2SO_4 and digested with water, was added to the filtrate in a 100-ml flask and made up to vol. with H_2O. A measured volume of this solution (40 ml $\equiv$ 0·05 per cent. of Al in the sample) was submitted to electrolysis and, after elimination of Fe, was filtered, evaporated to 50 ml, treated with 4 ml of NaOH soln. (40 per cent.) and 0·5 ml of 30 per cent. Na_2O_2, in water, boiled, filtered, made up to 100 ml, shaken and refiltered. A 50-ml portion of this solution was transferred by pipette to a 100-ml flask, neutralised with HCl to phenolphthalein, then treated with 0·4 ml of 5 per cent. HCl, 15 ml of freshly prepared 0·1 per cent. Eriochrome cyanine, 20 ml of buffer solution of pH 6·3 and H_2O to 100 ml. Extinction was measured against a control solution containing the reagents. S.C.I. ABSTR.

2669. **Separation of gallium, indium and germanium from other metals by ion exchange.** R. Klement and H. Sandmann (*Z. anal. Chem.*, 1955, **145** [5], 325–334).—A Dowex-50 cation exchanger in the H form was used to investigate the separation of In^{+++}, Ga^{+++}, Sb^{+++}, Pb^{++}, Cu^{++}, Zn^{++} and Fe^{+++}, with HCl in various concn. (0·1 to 1·5 *N*) as eluting agent. The quant. separations of both In and Ga from these elements are described and good results are reported. Indium and Ga can be readily separated from each other by first eluting In with 0·4 *N* HCl and then Ga with 1·3 *N* HCl. As it was found that Ge was not held by the cation exchanger, it should be possible to separate it from Pb, Cu, Zn and Fe, but difficulties arise in the presence of As and Sb, neither of which is retained. The quant. separation of Ge and Cu was successfully carried out. All separations can be carried out quickly. R. STERN

2670. **Yttrium—its gravimetric and colorimetric estimation with 8-hydroxyquinoline.** A. S. Murthy, T. P. Sarma and Bh. S. V. R. Rao (*Z. anal. Chem.*, 1955, **145** [6], 418–423).—The pptn. of Th with oxine is complete at pH 3·85; the pptn. of Y starts at pH 3·84 and is complete at pH 4·78. Owing to co-precipitation, however, separation of Th and Y by this method is not possible. For the gravimetric determination of Y, the oxinate is pptd. at pH 5 to 6; the ppt. is weighed after drying at 100° C for 4 to 8 hr., or after ignition to Y_2O_3. For volumetric determination, the ppt. is dissolved in 4 *N* HCl, treated with bromate - bromide and iodide, and titrated with standard $Na_2S_2O_3$. Titration with $Ce_2(SO_4)_3$ in 2 *N* H_2SO_4 is unsatisfactory.

For colorimetric determination of small amounts ($\simeq$ 10 mg) of Y_2O_3, the oxinate is washed thoroughly, dried, dissolved in acetone or CCl_4, and the extinction at 330 mμ or 340 mμ, respectively, measured. A. R. ROGERS

2671. **Photometric determination of cerium (IV) with veratrole.** H. N. Antoniades (*Chemist Analyst*, 1955, **44** [2], 34–37).—Procedures for the detection and determination of Ce^{IV} depend on the formation of a pink coloration (stable for $\simeq$ 8 min.) when a 5 per cent. v/v soln. of veratrole (*o*-dimethoxybenzene) in 95 per cent. ethanol is added to a soln. of $Ce(SO_4)_2$ in 1 *N* H_2SO_4. If faint, the colour can be intensified to orange by extraction of the complex with 1 ml of benzene or $CHCl_3$. A preliminary oxidation of the sample with $(NH_4)_2S_2O_8$ catalysed by Ag^+ is necessary, followed by complete decomposition of the excess of persulphate. *Quant. procedure*—Dissolve a weighed amount of sample and dilute to $\simeq$ 10 ml in a conical flask, add H_2SO_4 until the soln. is 2 *N*, then add 0·2 g of $(NH_4)_2S_2O_8$ plus 0·05 ml of 0·1 *M* $AgNO_3$, and boil for 10 min. Transfer the clear cool soln. to a 25-ml calibrated flask, dilute almost to the mark, add 0·4 ml of veratrole soln. and make up to 25 ml with water, mixing thoroughly. Transfer an aliquot to a 1-cm cell, allow the soln. to remain for exactly 5 min. and then measure the optical density at 350 or 475 mμ. The concn. of Ce^{IV} is calculated from a standard calibration curve. Beer's law is valid over the concn. 1×10^{-4} to 10×10^{-4} *M* of Ce^{IV}. W. J. BAKER

2672. **Hydrogen peroxide stabilised by titanium (IV) ions as a titrimetric measuring solution. Determination of cerium (IV) ions by direct titration.** M. T. Beck (*Acta Chim. Hung.*, 1955, **5** [3–4], 209–214).—A stable orange-red 0·1 *N* solution of peroxytitanic ion was prepared by adding 110 ml of aq. 1·0 *M* titanic sulphate to 5·65 g of 30 per cent. H_2O_2 dissolved in 500 ml of water and diluting to 1000 ml. This solution was used to determine 50 to 350 mg of $Ce^{\cdots\cdot}$ in 20 ml of 20 per cent. H_2SO_4. An adequate acidity is essential to prevent precipitation of basic titanium and cerium salts; heating to $\simeq$ 50° C increases the rate of reaction and facilitates the reading of the end-point. Indicators are not required. A determination based on the decolorisation of peroxytitanic sulphate by $Ce^{\cdots\cdot}$ was carried out in a Pulfrich photometer with filter S47 or S42. S.C.I. ABSTR.

2673. **Direct spectrographic analysis of cerium in cast iron.** W. R. Kennedy (*Applied Spectroscopy*, 1955, **9** [1], 22–26).—Flat-disc samples are sparked as cathode against a graphite counter electrode using an overdamped discharge from a Multisource at maximum capacity. The line pair Ce 4539·8 - Fe 4583·8 is suitable over the range 0·005 to 0·1 per cent. of Ce with an accuracy estimated at $\pm$ 20 per cent. at 0·005 per cent. and $\pm$ 10 per cent. at 0·05 per cent. P. T. BEALE

2674. **Complex colorimetry of rare earths.** L. Holleck, D. Eckardt and L. Hartinger (*Z. anal. Chem.*, 1955, **146** [2], 103–107).—To a 10^{-4} to 10^{-5} *M* soln. containing rare earths add ten times their weight of sulphosalicylic acid and five times their weight of aurinetricarboxylic acid. Warm, cool and make up to a known volume. Draw an absorption curve from 400 to 600 mμ and prepare a standard curve using lanthanum chloride. A complex is formed so that the lake is not pptd. Quantities up to 6×10^{-6} g per ml of rare earths can be determined. R. STERN

2675. **Solubility products of some rare-earth metal oxalates, and the instability constants of their complex sulphates.** I. M. Korenman (*Zh. Obshch. Khim.*, 1954, **24** [11], 1910–1916).—The solubility products of La, Ce and Pr oxalates are of the order 10^{-28}, as derived from measurements in 0·02 to 0·1 *N* HCl at 20° C. The solubility of the oxalates in H_2SO_4 exceeds that in HCl; this is ascribed to formation of complex ions, MSO_4^+, by the reaction $M_2(C_2O_4)_3 + 6H^+ + 2SO_4'' \rightleftharpoons 2MSO_4^+ + 3H_2C_2O_4$. The instability constants found were: $LaSO_4^+$, $3{\cdot}8 \times 10^{-4}$; $CeSO_4^+$, $1{\cdot}2 \times 10^{-3}$; $PrSO_4^+$, $4{\cdot}0 \times 10^{-3}$; $NdSO_4^+$, $1{\cdot}2 \times 10^{-3}$. R. TRUSCOE

2676. **Qualitative test for carbon dioxide.** W. W. Wendlandt and J. Bryant (*Chemist Analyst*, 1955, **44** [2], 52).—In the presence of CO_2 there is formed in a soln. of Na methoxide in methanol (1 g of Na dissolved in 50 ml of methanol) a voluminous white ppt. of Na methyl carbonate, which is insol. and does not settle out on being set aside. The test is claimed to be more reliable than the conventional lime-water procedure. W. J. BAKER

2677. **Micro-method of determining carbon in metals.** P. A. Kryukov and E. V. Rengarten (*Zh. Anal. Khim., SSSR*, 1955, **10** [1], 51–55).—The method suitable for the determination of microgram amounts of C is based on the measurement of the conductivity of the $Ba(OH)_2$ soln. used for absorbing CO_2. The O used is freed from traces of CO, hydrocarbons, etc., before entering the combustion tube by passing it into a vertical quartz tube at 600° to 700° C containing CuO, and then through an absorption tube containing 40 per cent. KOH solution. The method is suitable for determining 0·007 per cent. of C in Ti on a sample weight of 0·1 to 0·2 g, and for the normal percentages of C in steel on smaller sample weights. The apparatus is described and illustrated. G. S. SMITH

2678. **The rapid determination of small amounts of carbon in steel by the baryta shaking method.** T. Heczko (*Arch. Eisenhüttenw.*, 1954, **25**, 413–416).—The method consists in removing the CO_2 generated in the combustion of the steel sample with $Ba(OH)_2$ and titrating the unconsumed base with HCl. The apparatus described is simpler and cheaper than that used for the volumetric determination of C; it gives more accurate results for small contents of C and the same accuracy for higher values. A determination can be made in 10 to 15 min. CHEM. ABSTR.

2679. **Determination of carbon dioxide in coal.** R. K. S. Mehta and J. W. Whitaker (*J. Sci. Ind. Res., B, India*, 1955, **14** [3], 110–115).—Two methods are described for the determination of CO_2 in coal, using the 21-ml Haldane gas-analysis apparatus fitted with a small reaction vessel: (*i*) an absorption method, in which the CO_2 is liberated by HCl and absorbed in KOH, and (*ii*) an expansion method, in which the increase in gas volume, due to the liberated CO_2, is measured. The absorption method is applicable to all types of carbonates and in the presence of coal. The precision attainable is high and the time required for each estimation is $\simeq$ 1 hr. The expansion method is suitable for carbonate minerals in the absence of any gas absorbent such as coal, *e.g.*, carbonates of calcium, iron and magnesium. G. C. JONES

2680. **Volumetric analysis of silicon in elementary silicon.** S. Shinkai (*Japan Analyst*, 1953, **2** [5], 433–435).—Elementary Si reacts with conc. NaOH

soln. at 160° to 200° C to give an equiv. amount of hydrogen. A simple apparatus for the volumetric analysis was designed. Ferrosilicon reacts similarly with NaOH, but SiC does not. The results are reproducible, but slightly lower than those obtained by the gravimetric method. This difference appears to be due to different contents of SiC. The sample (1 g) is placed in a sealed tube and treated with a saturated soln. of NaOH (25 ml) on a sand-bath for 40 min. After being cooled, the tube is connected to a measuring tube and the vol. of H is measured. K. SAITO

2681. **Activation analysis of trace impurities in silicon using scintillation spectrometry.** G. H. Morrison and J. F. Cosgrove (*Anal. Chem.*, 1955, **27** [5], 810–813).—A method based on the use of neutron-activation analysis has been developed for the quantitative determination in a single analysis of many trace impurities in silicon and aluminium. The method entails little or no chemical manipulation, thus minimising the possibility of loss or contamination, and can be applied to other materials. After irradiation for three days at a flux of $\simeq 3{\cdot}4 \times 10^{12}$ neutrons per sq. cm per sec., samples are given a surface leach with equal vol. of saturated KOH soln. and 30 per cent. H_2O_2 before measurement of the impurities by gamma-scintillation spectrometry and other methods. Only those elements that give rise to radionuclides of half-life > 2 hr. or < 200 days can be determined easily under the conditions of the experiment. The method has a sensitivity of from 0·001 to 1 μg for most elements, with a standard deviation of about $\pm$ 1 per cent. in this range. The main part of the error appears to be due to the expected statistical fluctuation of radioactive decay, which can, however, be minimised by making a sufficiently large count.
K. A. PROCTOR

2682. **Photometric determination of low silicon contents in steel.** H. Wölk (*Arch. Eisenhüttenw.*, 1954, **25**, 333–336).—Comparison of the gravimetric and the photometric molybdosilicate and molybdenum-blue methods has indicated the applicability of the latter for the estimation of silicon contents of $< 0{\cdot}01$ per cent. in unalloyed steel. The preparation of the calibration curves and the methods employed for steel analysis are described in detail. The procedure can be carried out in 40 to 45 min. and the accuracy is $\pm$ 0·0005 per cent. J. IRON AND STEEL INST. ABSTR.

2683. **Determination of silica in ores, slags and refractories.** Methods of Analysis Committee, B.I.S.R.A. (*J. Iron & Steel Inst.*, 1955, **179** [4], 336–337).—The method of determining SiO_2 described earlier (*Anal. Abstr.*, 1954, **1**, 2373), which involves alkali fusion followed by a double $HClO_4$ dehydration, has been extended to cover other oxide-type materials, including iron ore, acid and basic slags, bauxite, and semi-silica bricks. Fusion with Na_2CO_3 followed by solution in HCl and dehydration with $HClO_4$ is satisfactory for most iron ores, slags and refractories, some of which yield to direct treatment with HCl for decomposition. Without major deviations in decomposition technique, however, the method cannot be applied to high-chromium, high-alumina and zircon-type refractories. Fusion with Na_2O_2, Na_2CO_3, Na_2CO_3–borax and NaOH was tried with varying degrees of success, but further work is needed before a standard can be prepared that gives reproducible results without contamination. W. ASHWORTH

2684. **Diphenylcarbazone as a reagent for the colorimetric determination of germanium.** G. S. Desmuk (*Zh. Anal. Khim., SSSR*, 1955, **10** [1], 61–62).—Addition of a drop of a saturated alcoholic solution of diphenylcarbazone to the yellow germanium - molybdate complex gives a purple colour similar to that in the reaction for Hg. The colour with Hg, as also the red colour given by diphenylcarbazone and ammonium molybdate, is destroyed on the addition of conc. HCl or H_2SO_4, but the colour of the germanium complex changes to deep blue, which is stable even in the presence of excess of acid. When ammonium molybdate solution is acidified before addition of a GeO_2 solution, or a neutralised sodium germanate solution is used, the blue colour is not produced. The reaction with diphenylcarbazone is sensitive to 0·1 μg of Ge in 0·03 ml. G. S. SMITH

2685. **Rapid method of approximate determination of lead in ores and concentrates.** L. B. Zaĭchikova (*Zavod. Lab.*, 1955, **21** [1], 27–29).—The method of Lang *et al.* (*Z. anal. Chem.*, 1933, **93**, 248) applied to a solution of 0·5 g of lead ore or concentrate, containing 0·3 to 3 per cent. of Pb, gives results that are low by 0·09 to 0·21 per cent. of the content. It is recommended that a correction of 0·15 per cent. be applied within this range. For higher contents the correction is variable and the method is unsuitable. G. S. SMITH

2686. **The analysis of metallic nickel. I. Determination of lead.** S. Yokosuka (*Japan Analyst*, 1955, **4** [2], 99–103).—Lead ($> 0{\cdot}005$ per cent.) in metallic Ni can be determined polarographically in *M* ammonium acetate soln. containing gelatin ($E_{\frac{1}{2}} - 0{\cdot}5$ V *vs.* the S.C.E.). The sample (10 g) is dissolved in dil. HNO_3 (1 + 1) ($\simeq$ 100 ml), evaporated three times with HCl and dissolved in warm ammonium acetate soln. For smaller lead contents (0·002 to 0·005 per cent.), PbS is pptd., together with a small amount of NiS, by adding a small amount of aq. NH_3 soln. to an acidic soln. (pH $\simeq$ 2) saturated with H_2S, and the ppt. is dissolved in HNO_3 and Br and treated as described above. Lead in Ni can also be extracted with dithizone from a basic soln. (pH 8 to 10) in the presence of a large excess of KCN and determined colorimetrically. The influence of Cu, Al, Fe^{III}, Sn and Bi can be eliminated by adding hydroxylamine and Na K tartrate. *Procedure*—The sample (10 g) is dissolved in dil. HNO_3 (1 + 1) (100 ml), evaporated to dryness to expel excess of acid and made up to 200 ml. A portion of this soln. is treated with hydroxylamine hydrochloride (10 per cent.) (1 ml), Na K tartrate (10 per cent.) (1 ml) and dil. aq. NH_3 solution (1 + 10) until $Ni(OH)_2$ begins to ppt. Sufficient KCN (10 per cent.) is added to convert all the Ni into the complex cyanide and the soln. is shaken with small portions (3 to 4 ml) of dithizone ($\simeq$ 6 mg per 100 ml of CCl_4) repeatedly until the CCl_4 layer remains green. The CCl_4 soln. are combined, made up to 30 ml, washed with aq. KCN soln. (1 per cent.) and water and submitted to colorimetric determination. **II. Determination of copper.** (*Ibid.*, 1955, **4** [2], 103–105).—The attempt to determine Cu (0·005 per cent.) in Ni polarographically in an ammonium acetate soln. was not successful. Copper in Ni is extracted with dithizone from an acidic soln. (pH $\simeq$ 1). No interference results from the presence of Pb (< 100 μg), Zn (< 50 μg), Mn (< 50 μg) and Cd (< 50 μg). When Fe > 30 μg is present, H_3PO_4 should be added to the soln. to be extracted.

The sample (10 g) is dissolved in HNO_3 and an aliquot is treated with H_2SO_4 until white fumes are evolved. The H_2SO_4 soln. is diluted with 0·1 *N* HCl and repeatedly extracted with dithizone. The CCl_4 layer is washed with water and the extinction coeff. is measured at 520 mμ. K. Saito

2687. ***m*-Nitrophenylarsonic acid as a polarographic reagent for titanium.** E. Van Dalen and R. P. Graham (*Anal. Chim. Acta*, 1955, **12** [5], 489–498).—Titanium is pptd. with *m*-nitrophenylarsonic acid and the nitrophenylarsonate is determined by polarographic reduction of the nitro group. The following conditions are necessary for quant. pptn. of a compound having a constant Ti:reagent ratio of 1:2—sulphate must be absent since it forms a complex with Ti, the pH of the medium must be 1·2 ± 0·4, ≮ 10 moles of reagent must be added for each mole of Ti, the Ti concn. must be ≮ 10 mg per litre. The reagent also precipitates Fe^{III}, Sn^{IV}, Zr^{IV}, Th^{IV}, Bi^{III} and uranyl salts. In the analysis of high-temp. alloys, Fe is first removed by electrolysis, and the same procedure would also remove Sn and Bi. *Procedure*—Dissolve 1·2 to 2·0 g of high-temp. alloy turnings, containing ≃ 2 per cent. of Ti, by boiling with 40 ml of 72 per cent. $HClO_4$, and dilute to 250 ml with "wash liquid" (aq. $HClO_4$ of pH 1·2). Dilute 25 ml of this soln. to 70 ml with wash liquid and electrolyse it at a mercury cathode with a current density of 0·15 amp. per sq. cm until a negative spot-test for $Fe^{\cdots}$ is obtained with SCN′. Adjust the soln. to a pH of 1·2 ± 0·4 by adding 7·5 *M* aq. NH_3, and add 50 ml of 0·8 per cent. aq. *m*-nitrophenylarsonic acid adjusted to pH 1·2 by the addition of conc. $HClO_4$. Set aside for 1 hr., filter on a Whatman No. 42 paper, wash the ppt. 3 times with wash liquid and dissolve it by adding, dropwise, 6 ml of a nearly boiling soln. of tartrate prepared by making 0·5 *M* tartaric acid strongly alkaline to phenolphthalein with conc. aq. NaOH soln. Adjust to the methyl red end-point with 5 *M* $HClO_4$, add 30 ml of 0·5 *M* K H phthalate and dilute to 100 ml. Polarograph the soln. with a Tinsley polarograph Type V with a countercurrent setting of 0, a galvanometer sensitivity of 20 micro-amp. per full-scale deflection, and a damping setting of 2. W. C. Johnson

2688. **Quantitative spectrographic analysis of zirconium for hafnium content.** G. Kryuger, R. R. Shvangiradze and T. A. Mozgovaya (*Zh. Anal. Khim., SSSR*, 1955, **10** [1], 20–27).—Spectrographic determination, with a medium dispersion spectrograph, of 0·02 to 15 per cent. of Hf in zirconium is carried out on a mixture of the oxides with graphite and sodium pyrophosphate (4 + 4 + 1) placed in the crater of a graphite electrode with a pointed graphite rod as counter electrode. Excitation is by a.c. arc, and the lines Hf II 2393·83 and Zr II 2392·68 A (for contents 0·01 to 1·0 per cent.) and Hf II 2417·69 and Zr II 2416·88 A (for contents 0·3 to 10 per cent.) are read. Standards are prepared from the pure oxides. The mean error is ≃ ± 5 per cent. G. S. Smith

2689. **X-ray spectrographic determination of hafnium in zirconium minerals and concentrates.** É. E. Vaĭnshteĭn, I. D. Shevaleevskiĭ and I. F. Shtauberg (*Zh. Anal. Khim., SSSR*, 1955, **10** [1], 14–19).—Published methods for the X-ray determination of Hf in minerals have possessed low sensitivity and low accuracy because it appeared necessary to use the relatively weak $L\beta_1$ and $L\gamma_1$ lines to avoid interference. With Hf in zirconium minerals it is recommended to use a working potential close to the excitation potential of the K lines of zirconium, enabling the stronger L lines to be used. A method is described which is suitable for hafnium contents of 0·2 to 2·5 per cent. with a mean error of ≃ ± 5 per cent. G. S. Smith

2690. **Analytical applications of the reaction of thorium with phenylphosphonic acid.** C. V. Banks and R. J. Davis (*Anal. Chim. Acta*, 1955, **12** [5], 418–431).—The following procedure is proposed for the gravimetric determination of $Th^{\cdots\cdot}$. To a soln. containing 0·02 to 0·2 g of $Th^{\cdots\cdot}$ add 150 ml of dil. HCl (1 + 3), heat to boiling point and add a 5-fold excess of 2·5 per cent. aq. phenylphosphonic acid; boil the soln. for 1 hr., dilute to 400 ml, adjust to pH 0·5 to 1·0 with conc. aq. NH_3 and set aside for a few hr.; filter off the ppt. on a filter crucible and dry it at 150° C. This gives $Th(C_6H_5PO_3)_2.3H_2O$ (38·796 per cent. of Th); a further drying at 250° C yields $Th(C_6H_5PO_3)_2.2H_2O$, at 500° C, $Th(HPO_4)_2.3H_2O$, and at 1200° C, $Th(HPO_4)_2$. Of 30 ions tested many give rise to high results and the following interfere seriously: $Tl^{\cdot}$, $Ti^{\cdots\cdot}$, $Fe^{\cdots}$, $ZrO^{\cdot\cdot}$, $Sn^{\cdots\cdot}$, $UO_2^{\cdot\cdot}$ and $SbO_3^{\cdot\cdot\cdot}$. Only small amounts of $Ce^{\cdots}$ and $La^{\cdots}$ should be present. Ionisation constants for phenylphosphonic acid are determined potentiometrically ($pK_1 = 0·91$, $pK_2 = 6·41$) and spectrophotometrically ($pK_1 = 0·96$, $pK_2 = 6·51$). Data for absorption spectra at 250 to 290 mμ for $C_6H_5PO_3H_2$, $C_6H_5PO_3H^{\cdot}$ and $C_6H_5PO_3^{\cdot\cdot}$ are reported. W. C. Johnson

2691. **Colorimetric estimation of thorium with carmine red.** N. Eswaranarayana and Bh. S. V. Raghava Rao (*Z. anal. Chem.*, 1955, **146** [2], 107–111).—On mixing carmine red with a solution containing Th, a violet complex results, which does not change colour in 48 hr. A pH of 2·5 and wavelength of 560 mμ are the most suitable for measurement. Of the elements commonly present only Fe^{III} interferes. The reaction obeys Beer's law up to 0·13 mg per ml. The ratio of Th to the reagent in the complex is found, from spectrophotometric data, to be 1:4. R. Stern

2692. **Estimation of thorium by organic reagents. VI. Use of some iodobenzoic acids.** S. K. Datta and G. Banerjee (*J. Indian Chem. Soc.*, 1955, **32** [3], 167–172).—The gravimetric estimation of Th can be accomplished by using the sodium salts of *m*-iodo-(**I**), 2-hydroxy-3:5-di-iodo-(**II**) and 2:3:5-tri-iodo-benzoic (**III**) acid, in the pH ranges 2·8 to 6·0, 3·2 to 6·0 and 3·0 to 6·0 for **I**, **II** and **III**, respectively. Most metal ions normally found with Th, with the exception of Fe and Zr, do not interfere. Double pptn. is necessary if Ni, Co, Cr or Mn is present, and for the quant. separation of Th from cerite earths and monazite sand. S.C.I. Abstr.

2693. **Thorium determinations in manganese nodules.** E. D. Goldberg and E. Picciotto (*Science*, 1955, **121**, 613–614).—The sample (1 g) is dissolved in HCl - $HClO_4$, the silica residue is dissolved in HF, and any remaining solid fused with Na_2CO_3. ^{234}Th is added to the combined soln. as a tracer to determine recovery. Th is then pptd. with $Fe(OH)_3$ by gaseous NH_3, the ppt. is dissolved in HF and lanthanum carrier is added to ppt. LaF_3, which also carries down the Th. This step is repeated to ensure complete separation of Th from Zr. The ppt. is dissolved in $Al(NO_3)_3$ - HNO_3 soln. and the Th extracted into mesityl oxide. The Th is stripped into water and extracted into a 2-thenoyltrifluoroacetone (TTA) - benzene mixture. The

residue from the TTA - benzene extract is dissolved in HCl and the Th measured colorimetrically as the thoron complex. Recoveries were from 50 to 80 per cent. H. F. W. KIRKPATRICK

2694. **Ammonia determination and sample preparation for mass spectrometer by a micro diffusion method.** S. W. Mayer, F. H. Kelly and M. E. Morton (*Anal. Chem.*, 1955, **27** [5], 837–838).—To permit the rapid analysis of large numbers of samples the authors have modified the method of B. Seligson and H. Seligson (*Brit. Abstr. C*, 1952, 72) to extend its range from 0·5 μg to 10 mg of nitrogen. They have also used the method to prepare samples for mass spectrometry, the sample being obtained in an interference-free form for treatment with hypobromite to produce nitrogen gas. Diffusion is carried out in a 30-ml bottle (30 mm × 70 mm), sealed by a rubber stopper holding a glass rod. The base of the rod is 20 mm from the bottom of the bottle and is broadened to hold 10 borosilicate-glass "helices," which are loaded with H_2SO_4 (50 per cent. for mg, 5 per cent. for μg range). *Procedure*—Place the sample in the bottle, add 8 glass beads and enough water (by pipette) to bring the liquid volume to 3 ml. Add 1·5 ml of saturated K_2CO_3 soln. and seal immediately. Rotate the bottle at 45 r.p.m. for 30 min., with its axis horizontal and 13 cm from the centre of rotation, while heating the bottle to a temperature of 65° ± 2° C with i.r. lamps. The ammonia is then determined by means of the Bock - Benedict modification of Nessler's reagent (Hawk *et al.*, "Practical Physiological Chemistry," 12th Ed., Blakiston, Philadelphia, 1947, p. 1230) with the Beckman DU spectrophotometer at the 418-mμ peak, after diluting as necessary. Recovery determinations showed a standard deviation of ± 2 per cent. for quantities > 10 μg and ± 0·2 μg for < 10 μg.
K. A. PROCTOR

2695. **Determination of phosphorus as quinoline molybdophosphate. Simplified precipitation of quinoline molybdophosphate by one precipitant.** U. Fernlund and S. Zechner (*Z. anal. Chem.*, 1955, **146** [2], 111–114).—An improvement on the authors' method (*Brit. Abstr. C*, 1953, 345) for the determination of small amounts of P is presented. The reagent (**I**) is made as follows—Dissolve $Na_2MoO_4.2H_2O$ (250 g) in H_2O (500 ml) and add conc. HCl (460 ml) and 30 per cent. H_2O_2 (1 drop). Add quinoline (28 ml) to HCl (1:1) (600 ml). Mix the two soln. Filter after 24 hr. *Procedure*—To a soln. containing P^v in HCl (0·9 to 1·6 *M*) add a few drops of $KClO_3$ soln. (6 per cent.), heat to boiling point and add 10 ml of **I**. Filter and wash the ppt. with 1 *M* HCl and then with H_2O. Wash the ppt. into a flask, and add an excess of standard NaOH soln. Titrate with standard HCl (phenolphthalein). Vanadium does not interfere. Practical details for the determination of P in Swedish iron ore are given. R. STERN

2696. **Colorimetric determination of phosphorus in coal.** L. Rodríguez Pire and C. García Gutiérrez (*Inst. Nac. Carbón, Bol. Inform.*, 1955, **4** [20], 84-101).—A comparison is made of the method of Belcher (*Fuel, Lond.*, 1950, **29** [10], 232) and that of Ellington and Adams (*Ibid.*, 1951, **30** [12], 272), with the molybdophosphate gravimetric method as reference method. For a wide range of coals and cokes, and with different colorimeters, both methods give good results in a short time, but the Ellington and Adams method is preferred since it takes less time; the error of weighing is of less importance, since 1 g of coal is used instead of 50 mg of ash, and the use of $SnCl_2$ which may give doubtful results owing to its instability is avoided.
D. LEIGHTON

2697. **Analytical chemistry of phosphates. I. New titrimetric determinations of pyro- and orthophosphates.** T. Kato, Z. Hagiwara, S. Shinozawa and S. Tsukada (*Japan Analyst*, 1955, **4** [2], 84–88).—Pyrophosphate is pptd. quant. with Zn acetate at pH ≃ 3·8. The ppt. is dissolved in aq. NH_3 soln. and titrated with sodium ethylenediaminetetraacetate soln. (**I**) at pH 10, with Eriochrome black T as indicator. The attempt to titrate pyrophosphate potentiometrically with caustic alkali soln. was not successful. Orthophosphate is pptd. with magnesia mixture in an ammoniacal soln., and the ppt. is dissolved in dil. HCl. The soln. is treated with a known excess of **I** at pH 10·8, the excess of which is titrated with $MgCl_2$, with Eriochrome black T as indicator. K. SAITO

2698. **Removal of phosphates with beryllium and EDTA.** J. Kinnunen and B. Wennerstrand (*Chemist Analyst*, 1955, **44** [2], 51).—The method depends on pptn. of PO_4''' by addition of excess of Be in the presence of ethylenediaminetetra-acetic acid (**I**), the excess of Be being simultaneously removed as $Be(OH)_2$. *Procedure*—Add an excess of **I** to an acid soln. of the sample, dilute to 200 ml, heat to 100° C, add ≃ 2 g of solid NH_4Cl plus an excess of 1 per cent. aq. $BeCl_2$ (0·7 mg of Be ≡ ≃ 1 mg of P), make the soln. slightly ammoniacal and boil for ≃ 2 min. Filter the cool soln. and wash the ppt. (PO_4''', As, Ti) with slightly ammoniacal 1 per cent. NH_4Cl. If the ppt. be large a double pptn. is advisable. The method can be used, instead of the tungstic acid pptn., for the determination of P and As in scheelite.
W. J. BAKER

2699. **Conditions for the formation of blue molybdo-phosphoric and -arsenic heteropolyacids.** M. L. Tsap (*Zavod. Lab.*, 1955, **21** [1], 10–17).—The max. absorption in the near infra-red of molybdenum blue and the blue molybdenum heteropoly complexes occurs in the ranges 700 to 725 mμ and 825 to 837 mμ, respectively. Determinations of the instability const. of the blue molybdophosphoric complex give a mean value of $0{\cdot}26 \times 10^{-7}$. The molar coeff. of absorption at 825 to 837 mμ of both the phospho- and the arseno-complexes is ≃ 2×10^4.
G. S. SMITH

2700. **Precipitation of quadrivalent vanadium by 5:7-dibromo- and 5:7-di-iodo-8-hydroxyquinoline.** I. P. Alimarin and V. G. Kryukov (*Zh. Anal. Khim., SSSR*, 1955, **10** [1], 56–60).—Acetone solutions of 5:7-dibromo- and 5:7-di-iodo-8-hydroxyquinoline added to $VOSO_4$ solution at pH 4 to 5 and at 50° to 55° C precipitate the V quantitatively as yellow $VO(C_9H_4ONBr_2)_2$ (after drying at 150° to 200° C) and yellow $VO(C_9H_4ONI_2)_2$ (after drying at 170° to 185° C), with conversion factors to V of 0·0760 and 0·0594, respectively. The ppt. are sol. in conc. acids, chloroform, amyl acetate and xylene, and are insol. in alkali. G. S. SMITH

2701. **Oxidimetric determination of vanadium (IV) with alkaline iodine solution.** G. S. Desmuk (*Chem. Ber.*, 1955, **88**, 615–617).—A new titrimetric procedure for oxidimetric determination of V^{IV} with iodine solution in aq. KI, at pH 9 to 10, adjusted by a borax - boric acid buffer, is described. The

excess of iodine is titrated with sodium arsenite. The simple method gives reproducible results (tabulated) which agree with those obtained by the classical permanganate method. *Procedure*—The V_2O_4 solution was obtained by reducing V_2O_5 with SO_2 and determining the content of V^{IV} by the permanganate method. To a known vol. of the above solution a known excess of iodine in aq. KI soln. was added and the air in the flask expelled by nitrogen. The pH was adjusted by means of a borax - boric acid buffer to pH 9 to 10. After 10 to 15 min. the unchanged iodine was titrated with sodium arsenite, with starch as indicator. 1 ml of N $As_2O_3 \equiv 0{\cdot}05095$ g of V.

S.C.I. Abstr.

2702. **Colorimetric determination of vanadium by means of a catalytic reaction.** V. A. Nazarenko and E. A. Biryuk (*Zh. Anal. Khim., SSSR*, 1955, **10** [1], 28–31).—A method based on the acceleration by V of the oxidation of aniline by chlorates activated by 8-hydroxyquinoline (*cf.* Szebelledy and Ajtai, *Mikrochemie*, 1938, **25**, 258; 1939, **26**, 72) is described. To 1·5 ml of the solution containing V as vanadate at pH 6·5 to 7·5 are added 0·1 ml of saturated sodium pyrophosphate solution, 2 ml of 5 per cent. aniline sulphate solution, 1 ml of saturated $KClO_3$ solution and 0·1 ml of 1 per cent. 8-hydroxyquinoline in N acetic acid. The solution is kept nearly boiling for 20 min. (with 0·005 to 0·020 μg of V) or for 5 min. (with $>$ 0·02 μg of V). It is then cooled and the colour intensity is compared visually with that of a series of standards. For higher contents of V, photometric determination at 430 to 470 mμ is used, with a blue filter. In amounts $<$ 10 μg, Mo, W, Re, Ti, As, Sb, Bi, Zr and Al do not interfere; Cu interferes in amounts $>$ 5 μg; Fe interferes seriously in the absence of pyrophosphate, but 10 μg can be tolerated in its presence. G. S. Smith

2703. **Colorimetric micro-determination of quinquivalent vanadium by means of a catalytic reaction.** G. Almássy and Z. Nagy (*Magyar Kém. Foly.*, 1954, **60** [4], 118–121; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 625).—A colorimetric method for the determination of 25 to 90 μg of V^V, in the presence of several hundred times as much Fe, Al, Mg, Ca, Ti, Co, Ni, Cu, Mn, Cr, Zn, Mo or U, is based on the oxidation of aniline by V^V in acid soln. in the presence of complex-forming oxalate ions. The colour of the green oxidation product is measured. The error is $\gtrsim$ 3 per cent. E. Hayes

2704. **Solubility of ammonium metavanadate in aqueous solutions of ammonium chloride.** V. V. Andreyev (*Zh. Obshch. Khim.*, 1954, **24** [10], 1730–1734).—The concn. of NH_4Cl required for complete salting-out of NH_4VO_3 varies according to the temperature, from 12·5° to 60° C, and to the initial concn. of NH_4VO_3, but is in all cases considerably below saturation. With aq. NH_4VO_3 saturated at 60° C and cooled to 12·5° C, 1·5 g of NH_4Cl should be added per 2·55 g of NH_4VO_3 in solution. The ppt. should be washed with 1·5 per cent. aq. NH_4Cl at 12·5° C. R. Truscoe

2705. **Separation of vanadium from titanium and iron by means of a cationite.** L. M. Orlova (*Zavod. Lab.*, 1955, **21** [1], 29–30).—The acid solution (pH $\simeq$ 1) containing V, Ti and Fe and excess of H_2O_2 to prevent reduction of V^V in the column is passed through a column of formaldehyde - resorcinol resin cationite (15 cm $\times$ 1 cm) at 2 to 3 ml per min. and the column is washed with water. The liquid containing V is boiled to destroy H_2O_2, treated with a few drops of $KMnO_4$ soln. (1 per cent.) to re-oxidise any reduced V and then with ammonium oxalate soln. (1 per cent.) to destroy the excess of $KMnO_4$. After addition of more acid, the cold solution is titrated with ferrous iron in the presence of phenylanthranilic acid. The Ti held by the column is removed by means of acid, the solution is treated with $KMnO_4$ to destroy H_2O_2, and the standard amount of H_2O_2 is added before determining the Ti colorimetrically. This method gives a complete separation of V and Ti.

G. S. Smith

2706. **Contributions to the chemistry of niobium and tantalum. XV. Determination by spectrum analysis of small amounts of tin in niobium pentoxide preparations.** G. Holdt and H. Schäfer (*Z. anal. Chem.*, 1955, **146** [1], 4–11).—A method for the quant. determination of Sn in Nb with the use of a carbon cathode is described. There are three stages of vaporisation; Sn and Nb are vaporised at the same rate in the middle stage, which is used for the determination. The addition of PbO (0·1 per cent. as reference element) was found to be advantageous. The lines 2863·32 A (Sn) and 2873·32 A (Pb) were used. Good results were obtained for SnO_2 between 0·001 and 3 per cent. R. Stern

2707. **Rapid absorptiometric determination of niobium in columbite, pyrochlore and other high-grade materials.** R. Pickup (*Colon. Geol. Min. Resour.*, 1955, **5** [2], 174–181).—In a previous paper (*Brit. Abstr. C*, 1953, 200) a method for the determination of Nb in low-grade materials, containing large percentages of Fe and Ti, was described in which the Fe was removed by chemical separation and interference due to Ti was suppressed. With high-grade materials no chemical separation is necessary, since the absorptions due to the relatively small amounts of Ti and Fe present are only very small fractions of that due to the Nb. The method is based on the absorption of the complex formed by H_2O_2 and Nb in H_3PO_4 - H_2SO_4 solution. The sample ($\simeq$ 50 mg) is fused with $KHSO_4$ (3 to 4 g) and the cooled melt is leached with hot H_2SO_4 (1:1). A little H_2O_2 is added and the solution is evaporated to copious white fumes, the fuming being continued for $\simeq$ 15 min. If the solution is cloudy on cooling, owing to pptd. $Fe_2(SO_4)_3$, 10 ml of H_2SO_4 (1:1) are added and the solution is again evaporated, but without prolonging the fuming. The acid concn. will thus be $<$ 98 per cent. and a small interference will eventually arise from the TiO_2 - H_2O_2 complex. (In the extreme case of a sample containing 40 per cent. of Fe_2O_3 and 40 per cent. of TiO_2 the interference will be equiv. to $\simeq$ 0·2 per cent. of Nb_2O_5.) The clear solution is added to 20 ml of H_3PO_4 (88 per cent. w/w), the mixture is made up to 100 ml with conc. H_2SO_4 (98 per cent. w/w), and divided into two aliquots. To one aliquot 0·1 ml of H_2O_2 (100 vol.) is added and the optical density is measured (with a Hilger - Spekker absorptiometer), at 365 mμ, relative to the unperoxidised aliquot. The accuracy of the method depends mainly on the precision with which the optical density of the Nb_2O_5 - H_2O_2 complex is measured. With the Spekker instrument fitted with a mercury vapour lamp and a Wood's-glass filter, the accuracy is probably better than $\pm$ 0·5 per cent. of Nb_2O_5 for materials containing 50 to 75 per cent. of Nb_2O_5. Interference of V, Cr and Ce is avoided by the addition of the H_2O_2 before evaporating to fuming. Traces of Pt cause rapid catalytic

decomposition of the Nb_2O_5 - H_2O_2 complex and must be removed by pptg. the earths with NH_3 in the presence of NH_4Cl. Molybdenum interferes, but its association with Nb - Ta ores is most unlikely. Both Ta and W interfere; ≃ 90 pt. of Ta_2O_5 or 17·5 pt. of WO_3 give the same effect as 1 pt. of Nb_2O_5 so that they are not serious factors unless they are major constituents of the ore. A procedure for the approx. determination of Ta_2O_5 is described.

J. M. JACOBS

2708. **Effects of heat and hydrochloric acid on the properties of some Nigerian minerals. I. Effect of heat on the magnetic properties of cassiterite. II. Effect of hydrochloric acid on certain Nigerian minerals and its use in the estimation of columbite.** W. N. MacLeod and M. P. Jones (*Colon. Geol. Min. Resour.*, 1955, **5** [2], 166–173).—**I.** The demagnetisation of magnetic cassiterite by heating is rapid at 1100° C and is accompanied by a striking change of colour from opaque black or dark brown to a translucent reddish-brown. **II.** The effects of leaching with hot conc. HCl, and of heating at 1000° C, on various Nigerian minerals associated with columbite are summarised. Columbite, unlike the associated minerals, is essentially unaltered by these treatments and this difference in behaviour forms the basis of a method for determining the columbite content of decomposed granite. The clay is removed from the sample by elutriation and the de-slimed residues are dried, screened into various standard sizes, and each fraction is passed through a magnetic separator. The magnetic fractions are leached with hot conc. HCl, to dissolve the ilmenite and iron oxides and demagnetise the zircon and thorite, until tests for Ti are negative. The columbite and the remaining magnetic minerals are separated magnetically from the demagnetised zircon and thorite and are then heated for 90 min. at 1000° C to demagnetise any cassiterite present and permit its removal by further magnetic separation. The columbite in the final fraction is usually contaminated with small amounts of monazite and xenotime (which are pale in colour and can be estimated visually), and with intergrowths of quartz with columbite and magnetite (which can be separated by heavy liquids). In general, this method gives lower values than those obtained by chemical determination of the niobium content of the rock.

J. M. JACOBS

2709. **Verification and perfection of a new method for the estimation of tantalum and niobium [in iron alloys].** B. E. Jaboulay (*Chim. Anal.*, 1955, **37** [6], 198–200).—A method is investigated in which Ta is separated from Nb by pptn. of the Ta from a boiling HCl - H_2O_2 soln. *Procedure*—A 0·2-g sample of ferrotantalum or ferroniobium is fused at red heat with 6 g of $KHSO_4$. The melt is dissolved in 200 ml of H_2O with 1 ml of HCl and 1 g of Na_2SO_3, and the soln. is boiled for 30 min. Tantalic and niobic acids, together with SiO_2, TiO_2, SnO_2, a little basic $Fe_2(SO_4)_3$, possibly ZrO_2, WO_3 and part of the MoO_3, are filtered off and washed (filtrate *A*). The residue is digested for 30 min. at 90° C with 10 ml of 20 per cent. yellow ammonium sulphide diluted to ≃ 150 ml, when the Sn, W, Mo and a few mg of Ta and Nb dissolve. The residue is filtered off, washed with H_2O, then with boiling 1 per cent. HCl and with H_2O (filtrate *B*), calcined, treated with a few ml of HF and 15 drops of H_2SO_4 in a platinum crucible, evaporated to fuming and fused again with 4 g of $KHSO_4$. The melt is dissolved and the soln. filtered as before (filtrate *C*, which is combined with filtrate *A* if necessary). The residue is again digested with ammonium sulphide (filtrate *D*). The combined filtrates *B* and *D* are acidified with HCl, 4 or 5 ml of Br are added and the soln. is boiled for 30 min. The soln. is filtered and the residue is digested with yellow ammonium sulphide. After filtering again, the residue of tantalic and niobic acids is washed with H_2O, then with a very dil. soln. of HCl and with H_2O, calcined and added to the main part. Potassium hydroxide (2 g) is fused in a nickel crucible and, after cooling, the mixture of Ta_2O_5 and Nb_2O_5 is added. The crucible is brought to a very dull red heat for a few min., and, after cooling, the melt is dissolved in ≃ 100 ml of cold H_2O. If Zr is absent, 15 ml of 12-vol. H_2O_2 are added and the soln. is poured immediately into 40 ml of HCl (sp. gr. 1·19). After being diluted to 800 ml, the soln. is kept nearly boiling for 50 to 60 min.; it is then filtered, and the residue is washed, calcined and weighed. The fusion with KOH and pptn. are repeated twice more, and finally the tantalic acid ppt. is calcined at 1000° C and weighed as Ta_2O_5. The filtrates are mixed, and are distributed in the 3 flasks, to each of which are added 3 g of Na_2SO_3 and a few drops of methyl orange. The soln. are neutralised with aq. NH_3 soln., acidified with 20 drops of HCl and boiled for 30 min. The soln. is filtered, and the residue washed, calcined and weighed as $Nb_2O_5 + TiO_2$. The TiO_2 is determined colorimetrically after being dissolved in HCl - H_2O_2, and the Nb_2O_5 is calculated by difference. During the estimation, tantalic and niobic acids form invisible or difficultly visible deposits on the walls of the vessels. They are detached by boiling with 2 *N* KOH soln., re-pptd. with HCl and combined with the main ppt. If Zr is present, 5 ml of 12-vol. H_2O_2, are added to the alkaline tantalate and niobate soln., which is poured into 10 ml of H_2SO_4 (sp. gr. 1·84). If the soln. is not perfectly clear, it should be diluted and filtered. The residue is then fused with $KHSO_4$, and extracted with H_2O to which a few drops of H_2SO_4 and H_2O_2 have been added. This soln. is then added to the main part. The greater part of the Ta and Nb is pptd. after boiling for 30 min. with Na_2SO_3 or SO_2 soln. The ppt. is filtered off, washed and re-pptd. as before. The combined filtrates contain all the Zr, most of the Ti and a little Ta and Nb. Some of the Ta and Nb is pptd. on evaporating to 100 to 120 ml. Five ml of 12-vol. H_2O_2 are added to the filtrate, and then 1 g of $(NH_4)_2HPO_4$. After being warmed to 50° to 60° C for a few min., the soln. is allowed to stand overnight. The ppt. of zirconium phosphate is calcined at 1000° to 1100° C and weighed as $4P_2O_5.5ZrO_2$. The filtrate is treated with SO_2 soln., neutralised with aq. NH_3 soln. and then boiled, when Ta, Nb and Ti are pptd. as phosphates. The residue is calcined, and then fused with 0·5 g of KOH. The melt is leached out with H_2O, 1 g of NH_4Cl is added and the soln. is boiled for ≃ 4 hr. The ppt. is filtered off, washed with a 1 per cent. NH_4Cl soln., calcined and added to the main ppt., which is fused with 2 g of KOH. The analysis is then continued as described above for Ta and Nb.

J. H. WATON

2710. **Applications of the electrochemical measurement of oxygen.** F. Todt (*Angew. Chem.*, 1955, **67** [9–10], 266–270).—The electrochemical method for determining oxygen in gases, waters, etc., is described fully, together with a number of specific applications of the method in industrial processes and scientific research. The following practical

applications of the method are discussed: (1) The determination of traces of O ($\simeq$ 20 μg per litre) in boiler-feed waters—A Ni cathode is used and the water under test flows through a monitor flask of Fe, which serves as anode. The current produced is sufficient to work a recorder without amplification. (2) The oxygen content of open waters (lakes)—A dipping electrode is used which has a measuring electrode of a special stable amalgam capable of giving a reliable reading within a few sec. of immersion, the dipping electrode being connected to a meter or continuous recorder. (3) Gas analysis—A system of lead anode - acid buffer solution - gold cathode is used with a magnetic stirrer and a built-in thermostat. Oxygen contents of 0·02 to 21 per cent. can be determined accurately by this method and variations in concn. can be followed. The presence of N, H, inert gases, hydrocarbons, N_2O, etc., does not affect the results. The method is highly sensitive and is useful for works control. (4) The change in oxygen concentration in reactions in which oxygen is evolved or taken up, *e.g.*, the oxygen taken up by divalent manganese or iron hydroxide under various conditions. (5) The de-aeration in penicillin production—The difficult problem of finding a suitable electrode for determining the oxygen content of the feeding solutions of the growing culture has now been solved. (6) Oxygen determinations in brewing processes (fermentation, and in the pressure and storage vats and in racking)—The great sensitivity of the method enables oxygen concn. of $<$ 10 μg per litre to be determined in the presence of 100,000 times the quantity of reducing substances. (7) The speed of respiration of micro-organisms—The method has been developed for observing the growth of yeasts, the oxidation of vitamin C and the destruction of staphylococcus by penicillin. (8) The continuous measurement of the oxygen liberated in the course of photosynthesis.

H. L. WHITEHEAD

2711. **The quick titrimetric determination of total sulphur in pyrites, roasted ores and flue dust with benzidine.** E. Eberius and E. Jahn (*Z. anal. Chem.*, 1955, **146** [2], 81–87).—The benzidine method for sulphate determination is critically reviewed, and the following method has been evolved to overcome most of the difficulties. *Procedure*—Fuse the sample (pyrites, 0·5 g; ores or flue dust, 2·5 g) with Na_2O_2 (15 g), dissolve in water, take an aliquot (after filtration, if necessary) and precipitate the sulphate with benzidine - HCl soln. in the presence of hydroxylamine hydrochloride. Filter (without the use of suction) after standing, and wash with 30 per cent. methanol. Wash the ppt. into the flask with water, heat to boiling and titrate with 0·1 *N* NaOH. The maximum error of the method is $\pm$ 0·4 mg of S. A method for the recovery of the used benzidine is given.

R. STERN

2712. **Micro-determination of sulphuric acid aerosol.** E. R. Gerhard and H. F. Johnstone (*Anal. Chem.*, 1955, **27** [5], 702–703).—A micro-determination of acid aerosols has been developed in which the particles are collected by a high-velocity impactor on a film impregnated with thymol blue. The preparation of this and other indicator films is described. The difference in light transmittance between the red acid trace and an adjacent yellow basic part of the film is measured by a photo-electric colorimeter attached to a low-power microscope, in which the eye-piece is replaced by a photocell. Reliable determinations of 0·01 to 0·2 μg of acid can be made as long as the quantity of acid collected is controlled to give essentially uniform traces. The method is not sensitive to acidic gases; alkaline gases, which tend to neutralise the droplets, affect the accuracy.

K. A. PROCTOR

2713. **A new volumetric determination of sulphate in Glauber's salt.** S. Shinkai (*Japan Analyst*, 1953, **2** [5], 432–433).—A known excess of $BaCl_2$ soln. ($\simeq$ 0·5 *N*) is added to a neutral sulphate soln. and the excess of Ba^{++} is pptd. by adding a known amount of Na_2CO_3 soln. The excess of Na_2CO_3 is titrated with HCl, with methyl orange as indicator. This method compares favourably with the Na rhodizonate method or the benzidine method.

K. SAITO

2714. **The photometric determination of tellurium with thiourea in nitric acid solution.** W. Nielsch and L. Giefer (*Z. anal. Chem.*, 1955, **145** [5], 347–349).—A solution containing 0·2 mg of Te per ml in 1 per cent. HNO_3 soln. was added to thiourea and various quantities of HNO_3 soln. and made up to 50 ml. The extinction coefficient was determined in a 1-cm cell after 15 min. and 14 hr. Reproducible results were obtained with HNO_3 concn. of 5 to 10 per cent., and were not affected by time, or by concn. of thiourea $>$ 10 per cent. Amounts of Te of 1 μg per ml could be determined. The thickness of the cell affected the result. Numerous ions interfere, and it is therefore advisable to separate the Te first or to mask these ions.

R. STERN

2715. **Potentiometric determination of dichromate ions and strong acids when present together.** I. E. Flis and Zh. L. Vert (*Zh. Anal. Khim., SSSR*, 1955, **10** [1], 44–46).—The Pt - H_2O_2 electrode (*Anal. Abstr.*, 1955, **2**, 2619) is applied to the titrations of mixtures of dichromate and H_2SO_4 and dichromate and HNO_3. A direct titration with alkali in the presence of H_2O_2 is unsatisfactory because of the formation of peroxidised chromium compounds, but accurate determinations of both constituents can be made potentiometrically by adding first a slight excess of alkali, then a few ml of 3 per cent. H_2O_2 solution and back-titrating with acid.

G. S. SMITH

2716. **The photo-electric colorimetric determination of tungsten by the use of stannous chloride and potassium thiocyanate.** H. Nishida (*Japan Analyst*, 1954, **3** [1], 25–29).—The acid concn. should be prescribed not for the final soln. with which the measurement of the light extinction is carried out, but for the soln. to which $SnCl_2$ is added, because the reduction of W is dependent on the concn. of H^+ and Cl'. A tungstate soln. ($<$20 ml) is treated with H_2SO_4 (5 to 10 ml), HCl (10 ml) and 2 *M* $SnCl_2$ at room temp.; KSCN (20 per cent.) (10 ml) is added and the soln. is made up to 100 ml. The extinction at 430 mμ remains constant for 2 hr. and is in accord with Beer's law for 0·1 to 3·0 μg of W per ml. Interference results from Ni ($>$ 10 μg per ml), Cr ($>$ 10 μg) and Co ($>$ 50 μg), but not from other elements, including Mo, Cu, Sn, Bi, Fe and Mn. This method is applicable to the estimation of W (0·005 to 3 per cent.) in ores.

K. SAITO

2717. **Quantitative separation by paper chromatography of microgram amounts of tungsten, chromium, vanadium, molybdenum and iron. I. Conditions and interfering factors.** A. Lacourt (*Ind. Chim. Belge*, 1955, **20** [3], 267–282).—A standard procedure has been devised whereby solutions, *e.g.*, of alloy-steels, containing $\leqslant$ 10 μg per 0·01 ml of

W, Cr, V and Mo in an excess of Fe, can be chromatographed on strips of Whatman No. 4 paper (dried over P_2O_5) so that the Fe is removed and the other four elements can be determined by direct titration on the paper (Mo, V) or by spectrophotometry of the spots (Mo, Cr, V, W). The solvent (100 ml) is a mixture of pentanol, benzene and conc. HCl (6:1:3), the developer (20 ml) is a mixture of pentanol (45 pt.) and 85 per cent. formic acid (55 pt.), whilst 17 ml of formic acid (85 per cent.) are used as a "contaminant" to ensure max. spot-separation and reproducibility. Aliquots (0·01 ml) of the original soln. in 85 per cent. v/v HCl (plus 1·12 per cent. of KOH if W is present) are dried for 10 min. by an i.r. lamp (38° C), then placed $\simeq$ 3 cm from the top of the paper strip (25 cm $\times$ 1 cm), and the chromatogram is run for 160 min. For both qual. and quant. analysis, the spots are located by revealing them on two of the eight strips in the glass cabinet, the remaining strips being cut for identification and determination of the separate elements by standard methods. In the presence of W, unconditioned strips can be used, but pre-saturation of the cabinet for $\simeq$ 68 hr. is necessary; the solvent used is the aq. layer, and the developing agent is the org. layer, obtained by shaking a mixture of water (155 ml), pentanol (60 ml), benzene (10 ml), conc. HCl (30 ml) and 85 per cent. formic acid (55 ml); only Mo and Fe migrate, but neither Cr nor V interferes in the subsequent spectrophotometric determination of W by the dithiol method. Reactions for identifying the spots are given.

W. J. Baker

2718. **Quantitative separation by paper chromatography of microgram amounts of tungsten, chromium, vanadium, molybdenum and iron. II. Quantitative study.** A. Lacourt (*Ind. Chim. Belge*, 1955, **20** [4], 399–414).—Full quant. and operating details are given for the paper-chromatographic separations and spectrophotometric procedures established in Part I (*Anal. Abstr.*, 1955, **2**, 2717) for solutions containing $\simeq$ 10 μg per 0·01 ml of W, V, Cr or Mo in either 85 per cent. v/v HCl or 85 per cent. v/v HCl + 1·12 per cent. w/v KOH (if W is present). The determination of W to within 2 to 3 per cent. is effected by spectrophotometry at 630 mμ of a butyl acetate soln. of the W - dithiol complex after elution of the chromatographed spot (W + Cr + V) for 2 hr. with 2 per cent. KOH. A separate extraction with butyl acetate is avoided by digesting the soln. on a steam-bath for 30 min. before rapid cooling and transfer to a 10-ml flask. The percentage of W is obtained by reference to standard calibration curves. Chromium is determined, either in the initial soln. or after elution of chromatographed spots with 2 *N* H_2SO_4, by measuring the intensity of the diphenylcarbazide - chromate coloration (*cf. Anal. Chem.*, 1952, **24**, 1016); interference from V and Mo is avoided by chromatographing from an 85 per cent. HCl solution only. The error is $\pm$ 1 to 2 per cent. The determination of V is effected by either (*i*) direct titration of the spot on the paper with aq. $Pb(NO_3)_2$ at pH 7, with diphenylcarbazide as internal indicator (the accuracy is within 4 per cent.), or (*ii*) direct photometry of the V spot $\simeq$ 30 min. after revealing the spots by spraying with NaOBr soln. and then, after i.r. drying, with acetic acid - oxine buffer; the V spot is black, the Cr spot becomes yellow on drying. This procedure, involving use of surface-concn. curves, is more accurate (mean error $\simeq$ 10 per cent.) when applied to the spot (V + Cr) obtained by partition chromatography, but $\gtrsim$ 3 μg of V or Cr should then be present. The determination of Mo to within 3 per cent. is by direct titration of the spot with 0·5 per cent. aq. $Pb(NO_3)_2$, with diphenylcarbazide as internal indicator (*Brit. Abstr. C*, 1952, 433), or alternatively, to within 1 per cent., by absorption measurements on the solution obtained by elution of the spots with twice-distilled H_2O and addition of a solution of KSCN in acetone (*cf. Anal. Chem.*, 1950, **22**, 328).

W. J. Baker

2719. **Organic co-precipitants. II. Co-precipitation of tungsten with organic co-precipitants.** V. I. Kuznetsov, V. N. Obozhin and E. S. Pal'shin (*Zh. Anal. Khim., SSSR*, 1955, **10** [1], 32–37).—Complete pptn. of W from acid solutions cannot be attained by the use of any one of the many precipitants that have been proposed, since W in acid solutions is present both as ions of varied character and as colloidal particles. The mixed precipitant described by Platunov (*Vest. Leningrad Univ.*, 1947, **12**, 101), methyl violet and tannin, is recommended. Complete pptn. occurs at a dilution of 1 in 10^{10}. The method is restricted to solutions containing no other elements pptd. by tannin.

G. S. Smith

2720. **Separation and determination of uranium.** I. Tsubaki (*Japan Analyst*, 1955, **4** [2], 77–79).—Several methods of separation and determination of U^{IV} and U^{VI} were re-examined and slight modifications are suggested. When U_3O_8 is treated with ammonium vanadate in dil. H_2SO_4, V^{IV} is obtained equiv. in amount to one-third of U_3O_8 ($2UO_3.UO_2$); this can be titrated with $KMnO_4$ soln. to give the amount of U.

K. Saito

2721. **Photometric determination of uranium in thorium.** L. Silverman and L. Moudy (*Nucleonics*, 1954, **12** [9], 60–62).—The determination of U by thiocyanate extraction of U into a non-aqueous solvent reduces interference of Th to $\simeq$ 1 per cent. of the U content. *Procedure*—Dilute the sample to 40 ml, add HCl to make $\simeq$ 10 per cent. acid by vol., add 8 g of KSCN and mix. Add $SnCl_2$ soln. (35 g in 100 ml of 20 per cent. HCl) dropwise to remove the red colour, with 1 drop in excess. Adjust the pH to 1·5 with 30 per cent. KOH soln. and transfer to a 125-ml separator. Add 21 ml of the dibutyl ether of tetra-ethylene glycol (**I**) and 2 ml of **I** - $SnCl_2$ reagent if the content of U is 0·1 to 3·5 mg, or 9 ml of **I** and 1 ml of the mixed reagent if the content of U is 0·02 to 0·1 mg; 4 ml of **I** and 1 ml of mixed reagent can be used for microgram quantities. Shake the soln. for 30 sec., allow the layers to separate, and discard the aq. layer. Filter the organic layer through dry Whatman No. 1 paper into a calibrated flask. Dilute to volume with **I**. After 2 hr. at 25° C read the optical density at 420 to 360 mμ. Amounts of Fe > 2 mg cause interference.

Chem. Abstr.

2722. **Spectrochemical analysis of fluorine by the use of band spectra of barium fluoride.** K. Fuwa (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [1], 14–17).—Several band spectra of BaF· were examined for use in the spectrochemical analysis of F. The sample (base substance, $BaSO_4$) is placed in a hole of a carbon electrode and a d.c. arc is struck (110 V, 8 to 10 amp.). The arc is focused on the slit of a spectrograph of the constant-deviation type and the image of the negative flame is observed or photographed. Bands of the green series (5000·6 A, 4950·8 A) are more sensitive than those of the infra-red or the extreme-red series, and are not affected by the band spectra of BaO. The

limit of detection is ≃ 0·1 per cent. of F and the intensity of the bands is approx. proportional to the concn. of F. The presence of phosphate decreases the sensitivity of the detection.
K. SAITO

2723. **Coulometric argentimetry. Quantitative determination of chloride, bromide and iodide ions.** P. S. Tutundžić, I. Doroslovački and O. Tatić (*Anal. Chim. Acta*, 1955, **12** [5], 481–488).—Halide ions are titrated with silver ions generated by the electrolytic oxidation of a silver anode of surface area 10 sq. cm. The cathode, which is separated by a sintered-glass plate, is of platinum foil, gauze or wire. A constant current of 4 to 100 mA is applied and the anolyte (60 ml) is stirred during the titration. For the titration of 0·01 *M* KCl the supporting electrolyte is *M* KNO_3 in 25 per cent. ethanol, for 0·0042 *M* KCl the electrolyte is 0·67 *M* KNO_3 in 35 per cent. ethanol and, for lower concn. of KCl, 0·25 *M* KNO_3 in 60 per cent. ethanol. Dichloro(R)fluorescein is used as indicator. The error varies from + 0·19 per cent. for 21 mg of Cl′ to + 1·12 per cent. for 1·77 mg of Cl′. For the titration of 0·01 *M* KBr the electrolyte is *M* KNO_3, for 0·001 *M* KBr the electrolyte is 0·5 *M* KNO_3, and for 0·0001 *M* KBr, 0·33 *M* KNO_3. Eosin is used as indicator. The error is + 0·17 per cent. for 48 mg of Br′ and + 0·83 per cent. for 1·2 mg of KBr. The conditions for the titration of I′ are similar to those for Br′; the error is + 0·17 per cent. for 76 mg of I′ and + 1·3 per cent. for 0·76 mg of I′.
W. C. JOHNSON

2724. **Use of Complexones in chemical analysis. XLIII. Modification of the iodimetric determination of manganese.** R. Přibil and J. Vulterin (*Chem. Listy*, 1954, **48** [8], 1132–1136).—In the presence of 1:2-diamino*cyclo*hexane-NNN′N′-tetra-acetic acid (**I**) and in weakly acidic solutions, Mn^{III} forms a stable intense-red complex which can be determined iodimetrically; the oxidation of Mn^{II} to Mn^{III} is achieved by means of PbO_2. Ferric ions, Cu^{++} and other cations become bound into stable complexes and do not interfere. The procedure has been successfully applied to a rapid determination of Mn in alloys and ores containing from 1 to 82 per cent. of Mn. *Procedure*—Decompose the sample by dissolving it in HNO_3 (or a combination of acids) or by alkaline fusion, filter off any SiO_2, treat an aliquot with a 0·1 *M* soln. of the disodium salt of **I**, adjust the pH to 5 with NaOH, add glacial acetic acid (10 to 20 ml) and Ca acetate soln. (10 ml), and oxidise the soln. with PbO_2 (0·3 to 1·5 g). Filter the mixture through sintered glass and titrate with 0·1 *N* $Na_2S_2O_3$ after adding KI (1 g). The complex of Mn^{III} with **I** exhibits max. absorption at 500 mμ and is well suited for the colorimetric determination of Mn in optimum concn. from 0·21 to 2·74 mg per 50 ml of soln.
G. GLASER

2725. **A rapid determination of manganese in iron and steel by oxidation with ammonium persulphate and titration with sodium thiosulphate.** T. Mukoyama, T. Ono and A. Shibata (*Japan Analyst*, 1955, **4** [2], 80–84).—Manganese in steel can be converted into $KMnO_4$ with $(NH_4)_2S_2O_8$ in the presence of Ag^+ and titrated with $Na_2S_2O_3$ soln. at room temp. The reaction between $KMnO_4$ and $Na_2S_2O_3$ appears to proceed at the molar ratio of 8:5. The $Na_2S_2O_3$ soln. should be standardised by the use of ferromanganese of a known manganese content. No interference results from the presence of Cr (< 2·5 per cent.), Co (< 3), Cu (< 0·5) or Ni (< 50). The preparation of the standard soln. is much simpler than that of other standard soln., such as sodium arsenite and vanadyl sulphate. *Procedure*—The sample (0·2 g) is dissolved in dil. HNO_3 (1 + 1) (30 ml), diluted with water (50 ml) and boiled with $AgNO_3$ (0·5 per cent.) (10 ml) and $(NH_4)_2S_2O_8$ (25 per cent.) (10 ml) for 1 min. The soln. is cooled, treated with NaCl soln. (1 per cent.) (10 ml) to ppt. Ag and titrated with 0·004 *N* $Na_2S_2O_3$. The standard $Na_2S_2O_3$ soln. can be kept with or without the addition of a stabiliser, *e.g.*, Na benzoate.
K. SAITO

2726. **Titrations with extractive end-points. II. The dichromate titration [of iron].** N. A. Gibson and R. A. White (*Anal. Chim. Acta*, 1955, **12** [5], 413–417).—Ferrous ions are titrated with 0·1 *N* $K_2Cr_2O_7$ in the presence of triphenylmethylarsonium chloride (**I**). At the end-point, $[(C_6H_5)_3CH_3]_2Cr_2O_7$ is formed and imparts a yellow colour to a layer of ethylene dichloride with which the soln. is shaken. By this means Fe^{++} can be titrated in the presence of coloured ions such as Co^{++}, Ni^{++}, Cu^{++}, Cr^{+++} and Mn^{++}. In solutions acidified with HCl, Zn^{++} and Sn^{++} form insol. compounds with **I**. *Procedure*—To 25 ml of a soln. ≃ 0·1 *N* in respect of Fe^{++} add *N* H_2SO_4 (≃ 200 ml), 5 per cent. aq. **I** (10 ml) and purified ethylene dichloride (5 ml). Titrate slowly with 0·1 *N* $K_2Cr_2O_7$ and shake the soln. when approaching the end-point. The ethylene dichloride is purified by shaking with aq. $KMnO_4$, then with conc. H_2SO_4 and finally fractionating.
W. C. JOHNSON

2727. **Estimation of ferric salts through photochemical reduction with oxalic and lactic acids.** G. G. Rao, G. Aravamudan and N. C. Venkatamma (*Z. anal. Chem.*, 1955, **146** [3], 161–166).—The photo-reduction of Fe^{+++} with oxalic acid is quant. under suitable conditions. The time for complete reduction increases with the amount of Fe^{+++}, but is independent of the acid concn. over the range 0·4 *N* to 1·6 *N* H_2SO_4. A u.v. lamp is more effective than a 1000-W tungsten lamp. If lactic acid replaces the oxalic acid, a decrease in the rate of reduction accompanies an increase in acidity. The reaction was studied in sunlight and in the light from a 1000-W tungsten lamp, but in the latter case the reduction is not rapid enough to be of use analytically. In all cases the Fe^{++} is estimated volumetrically with standard sodium vanadate soln., since unchanged reducing agent interferes if $K_2Cr_2O_7$ soln. is employed.
J. H. WATON

2728. **Functional-analytical groups for iron and bismuth.** N. M. Turkevich (*Zh. Anal. Khim., SSSR*, 1955, **10** [1], 47–50).—The thioamide group −C(SH):N− is a functional-analytical group for Bi (yellow coloration) and Fe^{+++} (red or red-brown coloration). Its specificity is conditioned by its capacity for tautomerisation, *e.g.*, HSCN, thiourea. The functional-analytical properties disappear in acylation [grouping −CS·N(CO·R)−]. Other functional groups for Fe^{+++} are −NH·C(:N·OH)− (lilac coloration) and −CO·C(SH) = (blue coloration). The non-acylated group −N= is a functional-analytical group for Bi in non-aqueous media, and gives difficultly soluble compounds, *e.g.*, those with thiazolidine, and $C_6H_5O_7Bi.NH_3$ (Turkevich, *Ukr. Khim. Zh.*, 1949, **15**, 243).
G. S. SMITH

2729. **Amperometric determination of iron and aluminium in bronzes.** Yu. I. Usatenko, G. E. Bekleshova, E. I. Grenberg, M. Ya. Genis and E. E.

Karpusha (*Zavod. Lab.*, 1955, **21** [1], 26–27).—The method is based on a titration of Fe^{++} with 0·05 *N* $K_2Cr_2O_7$, at an applied potential of + 1·0 V with reference to the saturated calomel electrode, using a rotating platinum micro-electrode, and a titration of Al^{+++} with NaF solution in the presence of Fe^{+++}. In both cases the end of the titration is shown by the disappearance of the Fe diffusion current. Bronze (1 g) is dissolved in 10 to 12 ml of dil. HNO_3 (1 + 1) and, if necessary, 4 to 5 ml of dil. HCl (1 + 1) and the solution is evaporated to fuming with 5 ml of conc. H_2SO_4. The cooled solution is treated with 25 to 30 ml of water and 5 ml of dil. HCl (1 + 1) and 4 g of zinc drillings are added in small portions to ppt. Cu and reduce Fe. The Cu is filtered off, the solution is made up to 100 ml and 20 ml are taken for amperometric titration of Fe. A further 20 ml is treated with 3 g of NaCl, 20 ml of ethanol and a drop of methyl orange soln. The electrodes are immersed without application of potential, the solution is neutralised with ammonia solution and the Fe is reduced with 5 per cent. ascorbic acid soln. added drop by drop. Excess of ascorbic acid is oxidised by 0·1 *M* ferric ammonium sulphate and the Al^{+++} are titrated with NaF solution. G. S. SMITH

2730. **Universal spectrographic method for the analysis of iron and steel.** S. Weisberger, F. Pristera and E. F. Reese (*Applied Spectroscopy*, 1955, **9** [1], 19–22).—Samples as small as 0·01 g are converted into oxide, mixed with graphite and arced on a graphite electrode in an H-V a.c. arc. Cr (< 2·3 per cent.), Mn (< 1·7 per cent.), Si, Co, Ni, Mo, Ti, Nb, V, Al and Cu (up to about 1 per cent.) and Pb, Sn and Ag (up to about 0·2 per cent.) are determined with an accuracy of $\simeq \pm 10$ per cent. of content. P. T. BEALE

2731. **Spectrographic analysis of plain carbon, low alloy and stainless steels.** R. S. Hullings (*Applied Spectroscopy*, 1955, **9** [1], 26–32).—The method employs the point-to-plane technique with an a.c. spark. By applying an "atomic dilution factor" to the highly alloyed steels it is claimed that common working curves can be used for all types and the accuracy is ± 1 per cent. of content, except for Cr in the range 11·5 to 13·5 per cent., when the accuracy is ± 4 per cent. of content. P. T. BEALE

2732. **Application of the high-voltage a.c. arc source to spectrographic analysis of steel.** T. Mitzuhashi, T. Nakashima and Y. Shiraishi (*Tetsu to Hagane*, 1953, **39** [11], 1277–1281).—An apparatus with 4400- or 2200-V arc sources is described; it can be used for spectrographic analysis of steel for Mn, Ti, Si, Ni, Cr and As, and gives results for small amounts that are impossible with spark methods. The method has high sensitivity and reproducibility within 3 to 8 per cent.; there is practically no continuous background and little loss of the specimen. J. IRON AND STEEL INST. ABSTR.

2733. **Determination of cementite in the presence of vanadium and molybdenum carbides.** N. M. Popova, A. F. Platonova and L. V. Zaslavskaya (*Zavod. Lab.*, 1955, **21** [1], 22–24).—The method is based on the stability of cementite to oxidation by H_2O_2 in ethanol. The sample of steel is subjected to the anodic dissolution process (Popova, *Ibid.*, 1945, **11**, 10) and the carbides are treated with 5 ml of ethanol and 5 ml of 30 per cent. H_2O_2, followed by heating at 50° C for 1 hr., cooling and repeating the treatment. The residue is analysed for Fe to give the cementite, and the solution is analysed for V and Mo. The completeness of the separation has been checked by X-ray analysis. G. S. SMITH

2734. **Quantitative inorganic paper-chromatography. Direct determination of cobalt by a scanning method.** S. V. Vaeck (*Anal. Chim. Acta*, 1955, **12** [5], 443–454).—A technique previously described (*Anal. Abstr.*, 1954, **1**, 942) for the determination of Ni is modified for the determination of Co. Four spots (10 µl) of the soln. of the unknown and 4 spots containing 0·8 to 2·0 µg of Co^{++} are applied to the paper, the spots are allowed to dry and the paper is kept in a humidity cabinet at 65 per cent. R.H. for 1 hr. The solvent is a mixture of 56 ml of acetone, 30 ml of *n*-butanol, 12 ml of aq. HCl (25 per cent.) and 2 ml of acetylacetone. The spots are sprayed with a 0·03 per cent. soln. of rubeanic acid (dithio-oxamide) in ethanol containing 5 per cent. of conc. aq. NH_3. The optical density of the spots is measured at 422 mµ at 2-mm intervals with the Photovolt densitometer, Model 525, or with the Beckman DU spectrophotometer equipped with a special adapter. The optical density is plotted against distance, and the amount of Co is proportional to the area under the curve. The method is applied to the determination of Co (0·2 per cent.) in nickel (error ± 5 per cent.) and in high-speed steel, and in the presence of equal amounts of both Ni and Cu. W. C. JOHNSON

2735. **Thioacetamide in the separation and compleximetric determination of cobalt and nickel.** H. Flaschka and H. Abdine (*Chemist Analyst*, 1955, **44** [2], 30–31).—Nickel or Co or both can be separated from other elements by one quant. pptn. with thioacetamide (2 per cent. w/v) in alkaline soln. and each can be afterwards determined by titration with 0·1 *M* aq. disodium ethylenediaminetetra-acetate (murexide indicator). *Procedure, for Ni alone*—Add 1 to 2 g of NH_4Cl and an excess of thioacetamide soln. to the neutral or slightly acid soln. and make strongly alkaline with conc. aq. NH_3. Heat to 100°C, boil for a few min. and filter through a sintered crucible (when the ppt. has settled completely). Dissolve the ppt. in 2 to 3 ml of a saturated soln. of Br in conc. HCl, dilute to $\simeq$ 75 ml, remove the excess of Br with ascorbic acid crystals, and then neutralise the soln. with conc. aq. NH_3 (methyl red indicator). Add 5 ml of NH_4Cl - aq. NH_3 buffer and titrate with the ethylenediaminetetra-acetate soln. *For Co alone or for ppt. containing Co and Ni*—Ppt., filter off and wash the sulphide as described above. Place the crucible in the pptn. beaker, add a few ml of aqua regia, boil gently for a few min., remove and rinse the crucible and dilute the soln. in the beaker to $\simeq$ 75 ml. Add 1 to 2 g of sodium acetate and make the soln. slightly alkaline with conc. aq. NH_3 (methyl red); finally complete the titration as described. Fe^{III} can be sequestrated with Tiron (disodium 1:2-dihydroxybenzene-3:5-disulphonate). The method is accurate to within $\simeq$ 0·5 mg of Ni or Co, when each is present alone. W. J. BAKER

2736. **Quantitative analysis without separation. XIV. Gravimetric analysis without separation for the systems Co - Cu and Pb - Hg.** N. Unohara (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [1], 38–40).—The thermal decomposition curves of $CoSO_4$, $CuSO_4$, $CuSO_4$ - $CoSO_4$, $PbCl_2$, and $PbCl_2$ - HgCl were studied with a thermobalance. The pyrolysis of $CoSO_4$ is promoted by the presence of $CuSO_4$. The determination of the amount of Cu from the weight decrease of the mixed sulphates on heating at 500° C and 790° C was unsatisfactory.

Mercury (> 60 mg), in the form of mixed chloride (≃ 600 mg) with Pb, can be determined from the weight decrease on heating at 100° C and 470° C. **XV. Gravimetric analysis without separation for the systems Co - Fe and Mn - Fe (sulphates).** (*Ibid.*, 1955, **76** [1], 40–41).—Similar experiments were carried out for the mixed sulphates of Co - Fe and Mn - Fe. Ferric iron can be determined from the weight decrease on heating at 350° C and 720° C only when its amount is greater than that of Co or Mn. K. SAITO

2737. **Composition of soluble complex compounds of nickel with dimethylglyoxime, obtained in the presence of oxidants.** L. S. Nadezhina and P. N. Kovalenko (*Zh. Obshch. Khim.*, 1954, **24** [10], 1734–1741).—The coloured co-ordination complex formed from $NiSO_4$ and dimethylglyoxime (H_2Dm) in the presence of the oxidants I, Br, $K_3Fe(CN)_6$, $(NH_4)_2S_2O_8$ and atm. O is the same in all cases, and has the composition $Ni(HDm)_3$. At $[NiSO_4] > 0{\cdot}001\ M$, sol. coloured complexes are not obtained, even with excess of oxidants, owing to pptn. of insol. $Ni(HDm)_2$, whilst with concn. of oxidant $> 0{\cdot}1\ M$ the coloration is discharged, owing to oxidation of H_2Dm. R. TRUSCOE

2738. **Detection of palladium with piaselenole.** M. Ziegler and O. Glemser (*Z. anal. Chem.*, 1955, **146** [1], 29–32).—To a test soln. in dil. HCl add 5 drops of a methanol soln. of piaselenole (0·5 per cent.). Palladium (1 pt. in 10,000) gives a copious yellow ppt., and 2 p.p.m. are detectable. Analysis shows the ppt. to be $Cl_2Pd(C_6H_4N_2Se)_2$. It is insoluble in most solvents. Cadmium interferes by giving a white ppt. Piaselenole is prepared by the action of H_2SeO_3 on *o*-phenylenediamine. R. STERN

2739. **Kinetics of the thermal dehydration of clays. III. Kinetic analysis of the clay minerals. IV. Interpretation of the differential thermal analysis of the clay minerals.** P. Murray and J. White (*Trans. Brit. Ceram. Soc.*, 1955, **54** [4], 189–203, 204–238).—A comprehensive theoretical consideration of the decomposition rate of a mixture of clay minerals having differing Arrhenius parameters shows that the decomposition - time curve of the mixture should enable the constituents to be identified and quantitatively estimated within certain limitations. The area (and not the height) of the peak of the rate of decomposition - temp. curve (analogous to the peak of the "differential thermal analysis" curve) is the true indication of the amount of mineral present. The method will require more investigation and detailed definition before it can be considered as an established practical analytical method. J. A. SUGDEN

2740. **Colloidal chemical determination of montmorillonite contents in bentonite.** A. Buzágh and K. Szepesi (*Acta Chim. Hung.*, 1955, **5** [3–4], 287–298).—A method of separating montmorillonite from other clay minerals (kaolinite, illite, beidellite) by the difference in stability of their suspensions was investigated. The difference in stability, increased by the addition of dehydrating agents (*e.g.*, ethanol) and conversion of the clay minerals into their alkali salts, proved sufficient for the separation and determination of sodium montmorillonite. The test suspensions (10 ml, 2 per cent.) were treated with 10 ml of Na_2CO_3 soln. of known concn., and compared with an electrolyte-free suspension by macroscopic sedimentation. Residues of sodium montmorillonite remained stable in alcoholic suspension, whereas the other minerals were sedimented by centrifuge. Gravimetric determination of the total montmorillonite contents in various types of bentonite and clay mixtures was achieved by converting alkaline-earth into alkali montmorillonites with those alkali salts that form sparingly soluble compounds with alkaline-earth ions (*e.g.*, sodium carbonate, fluoride, phosphate and oxalate). Samples of dry bentonite (1 g), mixed with 2 to 3 ml of H_2O, were treated with 5 per cent. Na_2CO_3 soln. (optimum 4 per cent. Na_2CO_3 on dry substance) and evaporated to dryness. The residue was suspended in 100 ml of water, the suspension was centrifuged and the supernatant liquid decanted, evaporated, dried and weighed. The hygroscopic product was found to be pure montmorillonite. The method is sufficiently accurate to serve as a basis for a process of activating bentonites. S.C.I. ABSTR.

2741. **Observations on the measurement of pH values of soft brown coal.** H. Jacob (*Chem. Tech., Berlin*, 1955, **7** [3], 163–164).—The applicability and errors of colorimetric and electrometric methods for measuring pH values of soft brown coal are discussed. Of the different types of electrodes, hydrogen, quinhydrone, antimony, bismuth and glass, the last has the widest application for brown coal as it is the only one not affected by certain electrode poisons normally present in coal. R. J. MAGEE

See also Abstracts 2613, 2623, 2746, 2913.

3.—ORGANIC ANALYSIS

2742. **Rapid methods in the organic microanalytical laboratory.** W. Schöniger (*Angew. Chem.*, 1955, **67** [9–10], 261–265).—A review is given of the development of more rapid methods for the microanalysis of organic compounds (including both the elementary analysis and the determination of the functional groups) and of the apparatus (including the modern riderless air-damped special balances) used for the purpose. Detailed descriptions are given of some of the most rapid methods for the micro-estimation of C, H, N, O (directly), S and halogens, and for the micro-determination of the following functional groups: methoxyl, N-alkyl, active hydrogen, hydroxymethyl and C-methyl, and primary amino. The methods are discussed and compared and the time taken to effect the estimations is given. Other ways of saving time in the work which are discussed are the pre-drying of samples, the organisation of the laboratory, and the use of calculating machines for working out the results. H. L. WHITEHEAD

2743. **Simultaneous determination of total carbon and carbon-14 activity.** J. D. Gabourel, M. J. Baker and C. W. Koch (*Anal. Chem.*, 1955, **27** [5], 795–797).—The standard Pregl combustion procedure is unsatisfactory for determining the activity of ^{14}C-labelled compounds because of radioactive cross-contamination between consecutive samples; wet-combustion methods often yield low values for C. An alternative tube packing is described which gives accurate carbon and hydrogen contents without cross-contamination in the subsequent ^{14}C determination. The combustion gases pass through 7 cm of platinum gauze and 11 cm of granular quartz, both at 900° to 950° C, and then through 4 cm of very pure MnO_2 on platinised asbestos and 3 cm of silver wool, both at 175° C. The temp. of the movable furnace is raised from 300° to 850° C in the course of the analysis. The standard oxygen

flow rate is 4 to 5 ml per min. for a 3 to 6-mg sample. A. R. ROGERS

2744. **Correction factors for comparing activities of different carbon-14-labelled compounds assayed in flow proportional counter.** M. L. Karnovsky, J. M. Foster, L. I. Gidez, D. D. Hagerman, C. V. Robinson, A. K. Solomon and C. A. Villee (*Anal. Chem.*, 1955, **27** [5], 852–854).—Correction factors have been reported to be necessary (Crane and Ball, *J. Biol. Chem.*, 1951, **188**, 819; Topper and Hastings, *Ibid.*, 1949, **179**, 1255; Yankwich and Weigl, *Science*, 1948, **107**, 651) in making conversions of the activities of organic substances, counted as such, to equivalent activities determined by counting the ^{14}C as barium carbonate; end-window Geiger-Müller counters were used. The authors have made measurements with a windowless gas-flow proportional counter (Robinson, *Anal. Chem.*, 1950, **112**, 198) and a mixture of argon with 5 per cent. of CO_2. With this counter and with thin samples mounted on stainless-steel planchets, correction factors are found under routine conditions to be significantly lower than those previously reported and approximate to unity. K. A. PROCTOR

2745. **Determination of traces of sulphur in organic compounds. Vertical-furnace method.** J. A. Hudy and R. D. Mair (*Anal. Chem.*, 1955, **27** [5], 802–805).—Existing methods of determining traces of S in organic liquids suffer from lack of sensitivity and precision. A method has been developed which is suitable for the concn. range 1 to 100 p.p.m. The combustion gases issuing from an improved version of the vertical V_2O_5-packed furnace of Wilson and Straw (*Brit. Abstr. C*, 1950, 399), burning 15 to 30 g of sample per hour, are absorbed in H_2O_2 soln.; the excess of peroxide is decomposed with platinum catalyst, and the resulting sulphate is measured by the conductimetric method of Polsky (*Brit. Abstr. C*, 1948, 33). The method has been applied extensively to terpenes, aromatic hydrocarbons and alcohols. It has an accuracy and precision of $\simeq$ 1 to 2 p.p.m. of S. A. R. ROGERS

2746. **A rapid micro-determination of mercury in organic substances containing halogen.** T. Sudo, D. Shimoe and F. Miyahara (*Japan Analyst*, 1955, **4** [2], 88–91).—To avoid possible loss of mercury halides during the decomposition of org. substances, a simple combustion method is suggested. The sample (5 to 10 mg) is placed in a combustion tube filled with CaO and burnt in a current of air (5 ml per min.) at 370° $\pm$ 10° C for 20 min. Mercury is then collected in a bubbler containing conc. HNO_3 (1·5 ml) with a further passage of air (10 ml per min., for 10 min.). The dissolution of Hg is completed by the addition of a small amount of $NaNO_2$, the excess of which is decomposed with $KMnO_4$. The soln. is treated with H_2O_2 and titrated with 0·005 *N* KSCN, with iron alum as indicator. The presence of Cl or Br does not interfere. The time required for an estimation is $\simeq$ 35 min. K. SAITO

2747. **Colour reactions for unsaturated carbonyl compounds. I. *p*-*N*′-Sulphohydrazinoazobenzene as colour reagent.** S. Hünig and J. Utermann (*Chem. Ber.*, 1955, **88**, 423–429).—On the basis of qual. reactions and absorption spectra it is shown that the colour reactions between *p*-N′-sulphohydrazinoazobenzene (**I**) and unsat. carbonyl compounds depend on the number of double bonds conjugated with the carbonyl group. A regular variation of the colour and widening bands in the absorption spectra indicate the increasing number of double bonds in the side-chain. Aldehydes and ketones of the furan series were found particularly suitable for the study of these reactions. Furylpolyenal with one vinylene group shows blue with an excess of **I**, with two a greenish-blue, with three green, with four olive-green, and with five a greenish-brown colour. A solution containing 5 ml of $2·2 \times 10^{-5}$ *M* **I** (m.w. 399·5) and 5 ml of $2·2 \times 10^{-3}$ *M* 5-furylpentadienal (m.w. 148·1) is treated with 1 ml of methanolic HCl (1 vol. of conc. HCl to 1 vol. of methanol) and measured against a solution without **I**. The speed of colour formation at the absorption maximum is determined and readings are taken at times of constant extinction. Since the colour solutions are fairly stable, the reaction is suitable for quant. determinations. S.C.I. ABSTR.

2748. **Chromatographic analysis of hydrocarbon mixtures.** B. W. Bradford, D. Harvey and D. E. Chalkley (*J. Inst. Petrol.*, 1955, **41** [375], 80–88).—The principal chromatographic methods employed in the analysis of hydrocarbon mixtures, and recent developments that provide powerful new techniques in this field, are reviewed. Apparatus and techniques for dealing with liquid and with gaseous samples are described, with examples. No general deductions can yet be made as to the accuracy and reproducibility attainable through these techniques; for routine analysis the problem is different, and data are being accumulated on performances under standardised conditions over long periods. J. M. JACOBS

2749. **Refractometric analysis of ternary systems [of hydrocarbons, etc.].** B. V. Ioffe and A. G. Morachevskiĭ (*Zh. Anal. Khim., SSSR*, 1955, **10** [1], 3–13).—Two general methods of refractometric analysis of ternary systems (of hydrocarbons, etc.) are considered. The dispersiometric method is based on measurements of refractive index at two wavelengths, and the extraction method is based on determinations of the index before and after extraction of a component by a suitable reagent or solvent. Organic compounds can be classified as compounds of high dispersion ($\nu_{FCD} > 27$), *e.g.*, aromatic compounds and heterocyclic compounds of aromatic character, with not very complex aliphatic radicals, aliphatic and alicyclic compounds containing two or more conjugated double or triple bonds, iodine derivatives of all classes, and the simplest organometallic compounds of Pb, Hg, Cd and Zn, and compounds of low dispersion ($\nu_{FCD} < 22$), *e.g.*, compounds which do not contain a multiple C–C bond (paraffin and cycloparaffin hydrocarbons, alcohols, ketones, aldehydes, acids, ethers, esters, amines, amides, nitriles, chlorine derivatives, and mono-bromine derivatives), and most compounds containing one multiple C–C bond, also water. The analysis of a ternary system by the dispersiometric method is practicable if two components occur in one of these groups and differ sufficiently in refractive index, and the third occurs in the other group. The method usually requires the prior construction of a triangular diagram, but if, as with hydrocarbon systems, none of the components is strongly associated and no chemical interaction occurs, the composition of the mixture can be determined from the refractive index measurements and a knowledge of constants derived from data for the binary systems and expressing deviations from additivity. The calculation involves the solution of a system of three linear equations, and the results are correct to

± 1 per cent. for mixtures of aromatic hydrocarbons with naphthenes and paraffins. The extraction method is discussed in relation to the mixture of an aromatic and a saturated hydrocarbon with an aliphatic alcohol. A preliminary study expressed by means of triangular diagrams of the relation between refractive index and composition is required. The alcohol is removed by shaking with 75 per cent. sulphuric acid. Results accurate to ± 0·2 per cent. are attainable.
G. S. SMITH

2750. **Polarographic reduction of ethers [and esters].** M. I. Bobrova and A. N. Matveyeva (*Zh. Obshch. Khim.*, 1954, **24** [10], 1741–1749).—Vinyl ethers not possessing conjugated double-bond systems do not undergo polarographic reduction (background electrolyte 0·1 *M* tetramethylammonium iodide in 75 per cent. ethanol). Methyl acrylate, methacrylic acid, and methyl and butyl methacrylates can be determined polarographically (background electrolyte 0·1 *M* tetramethylammonium iodide in 50 per cent. ethanol). R. TRUSCOE

2751. **Colorimetric determination of lipid and organic peroxides.** A. M. Siddiqi and A. L. Tappel (*Chemist Analyst*, 1955, **44** [2], 52).—A rapid iodimetric method giving results that are stoicheiometrically related to the organic-peroxide content is described. *Procedure*—To 4 ml of a methanol soln. of the sample add 4 ml of a (1 + 2, by vol.) mixture of $CHCl_3$ and acetic acid, followed by 2 ml of a saturated soln. of KI in methanol. Pass a fine stream of nitrogen through the liquid in a test-tube in a water bath (37° C) for ≃ 15 min. and then determine the light-absorbancy at 500 to 570 mμ, with a green filter. The peroxide concn. is obtained from a calibration curve for similarly treated solutions having benzoyl peroxide concn. from zero to 0·0003 *M*, over which range Beer's law is valid. W. J. BAKER

2752. **Improved test for formaldehyde.** F. Feigl and L. Hainberger (*Chemist Analyst*, 1955, **44** [2], 47–48).—The sensitivity of the Eegriwe chromotropic acid test for formaldehyde is increased to 0·025 μg, or 1 in 2×10^6, by the rigorous exclusion of H_2O, *e.g.*, aq. formaldehyde is evaporated to dryness with aq. NH_3 soln. and the test is made on the residue of hexamethylenetetramine. For materials that liberate formaldehyde on pyrolysis or heating with conc. H_2SO_4, *e.g.*, synthetic resins, the following procedure is adopted. Place the sample (≃ 0·1 mg) in the bottom of a small glass tube and over it suspend one drop of freshly-prepared chromotropic acid reagent, by means of a glass rod passing through a stopper; immerse the tube ≃ 1 cm in an oil-bath at 170° to 180°C for a few min.; in the presence of formaldehyde the hanging drop turns purple. W. J. BAKER

2753. **Specific reaction for formaldehyde.** G. Vanag and É. Vanag (*Zh. Anal. Khim., SSSR*, 1955, **10** [1], 63–64).—A test with 2-nitroindane-1:3-dione is described. To 5 to 10 mg of the reagent in a test-tube are added 1 to 2 drops of the solution containing formaldehyde and, after 15 min. at room temp., 1 ml of conc. H_2SO_4. After a gentle heating, the yellow colour of the solution changes to a green fluorescence in the presence of formaldehyde. At a dilution of 1:33,000, 3 μg can be detected in 0·1 ml of solution. The reaction is not given by acetaldehyde, paraldehyde, chloral hydrate, acraldehyde, propion-, *iso*butyl-, *n*-hept-, croton-, benz-, *o*-, *m*- and *p*-nitrobenz-, salicyl-, anis- and hydrocinnam-aldehydes, nor by any compounds related to formaldehyde except hexamethylenetetramine. G. S. SMITH

2754. **Determination of a small amount of acetaldehyde in vinyl acetate.** Y. Arikawa (*Japan Analyst*, 1953, **2** [5], 436–439).—Acetaldehyde (0·005 to 0·2 per cent.) in vinyl acetate is quantitatively extracted with $NaHSO_3$ soln. (1 per cent.) through the formation of an addition compound [CH_3·CH(OH)·SO_3Na]. This is decomposed in a basic soln. and the liberated $NaHSO_3$ is titrated iodimetrically. No interference results from the presence of < 5·7 per cent. of acetic acid. Acetone and crotonaldehyde form similar addition compounds and interfere with the result. *Procedure*—The sample (20 ml) is shaken with 1 per cent. $NaHSO_3$ soln. containing 10 per cent. of NaCl (to avoid the formation of an emulsion) and the water layer is separated. The excess of $NaHSO_3$ is oxidised with 0·1 *N* iodine soln., then the aq. soln. is treated with $NaHCO_3$ to give a pH value ≃ 8 and titrated with 0·01 to 0·1 *N* iodine soln.
K. SAITO

2755. **Ultra-violet determination of combined methyl *iso*propenyl ketone in polymers.** J. J. Pepe, I. Kniel and M. Czuha, jun. (*Anal. Chem.*, 1955, **27** [5], 755–758).—The methyl *iso*propenyl ketone (**I**) content of copolymers containing **I** may be determined spectrophotometrically. The sample is dissolved in $CHCl_3$ and pptd. with methanol, then redissolved in $CHCl_3$, filtered through a Seitz apparatus under pressure, and examined in 1-cm cells at 290 mμ with a slit width of 0·5 mm in a Beckman spectrophotometer; $CHCl_3$ is used as blank. A correction for the u.v. absorption due to the other components of the copolymer (namely butadiene, or butadiene and vinyl cyanide) is subtracted. The method is rapid and reproducible to within 0·4 per cent. Antioxidants such as phenyl-2-naphthylamine interfere. A. R. ROGERS

2756. **New solvent system for separating monocarboxylic acids (C_2 to C_{16}) and dicarboxylic acids (C_2 to C_{22}).** V. Zbinovsky (*Anal. Chem.*, 1955, **27** [5], 764–768).—Silicic acid columns may be used for the quant. separation of all the saturated aliphatic monocarboxylic acids from C_2 to C_{14} and dicarboxylic acids from C_2 to C_{22}. A mixture of 2-methoxyethanol - water (9:1) is used as internal phase, and either Skellysolve B or dibutyl ether or mixtures of these as external phase. Samples of ≃ 5 mg of total acids are handled. The time required for a run ranges from 1 to 24 hr., according to the number of acids present. Recoveries of individual acids range from 97 to 103 per cent.
A. R. ROGERS

2757. **Use of polythene in separation of fatty acids by reverse-phase chromatography.** T. Green, F. O. Howitt and R. Preston (*Chem. & Ind.*, 1955, [21], 591–592).—The replacement of the kieselguhr - liquid-paraffin stationary phase (**I**) by powdered polythene (200 mesh B.S. sieve) in the reverse-phase chromatographic column of Martin and Howard (*Brit. Abstr. C*, 1950, 487) gave satisfactory results in the separation and estimation of unsaturated fatty acids with solvents of high acetone content, and avoided the tendency of **I** to lose liquid paraffin. The process works satisfactorily at room temp. for the lower acids (C_6 to C_9), but a temp. of 35° C is recommended for the higher acids (C_{10} to C_{20}). S.C.I. ABSTR.

2758. **Infra-red evaluation of sodium salts of organic acids.** E. Childers and G. W. Struthers (*Anal. Chem.*, 1955, **27** [5], 737–741).—The determination of the lower aliphatic carboxylic acids by i.r. absorption is difficult because of the effects of hydrogen-bonding. The i.r. spectra of the sodium salts of the monobasic acids from acetic to caproic and of the dibasic acids from oxalic to pimelic are given for the range 7 to 15 μ. The absorption bands show a marked degree of specificity, and can be used for both qual. and quant. evaluation of acid mixtures. *Procedure*—Neutralise an aq. soln. of the mixed acids to phenolphthalein with 25 per cent. aq. NaOH, evaporate to a thick slurry, dilute with acetone, filter, and weigh the ppt. after drying it at 110° C for 3 hr. Prepare a mull of the anhyd. salts (0·4 g) in white mineral oil (2 ml), and measure the i.r. spectrum. Naphthalene (0·3 per cent.) may be used as an internal standard as a reference for cell thickness. By using a standard curve, a relative precision of 4 per cent. is claimed. The time required for a complete analysis of a single sample is 4 hr., including the drying time for the salt. A. R. ROGERS

2759. **Paper chromatography of higher fatty acids.** V. Kobrle and R. Zahradník (*Chem. Listy*, 1954, **48** [8], 1189–1196).—Higher fatty acids containing an even number of carbon atoms (10 to 22 and 26) were readily separated on filter-paper impregnated with a 12 per cent. soln. of a triglyceride (vegetable oil) in toluene as the stationary phase and with aq. alcohol as the mobile phase. The spots were detected by treating the chromatogram with aq. $AgNO_3$ soln. and drying it at 150° C for a few min. The influence of the papers used, the solvent systems, the temp. and the developing method on the R_F values of the individual acids is discussed and these values for the various experimental conditions are given. A linear relationship between the R_F values and the number of carbon atoms in the molecule of the fatty acid was established and quantitatively defined by the expressions $R_F = a + bn$ for saturated C_{10} to C_{20} acids, and $R_F = a + b(n - 2)$ for unsaturated acids with one double bond and for dicarboxylic acids, where n is the number of carbon atoms, and a and b are empirical constants. For Whatman No. 1 paper impregnated with olive oil, and for 75 per cent. aq. ethanol as the mobile phase, $a = 1{\cdot}42$, and $b = -0{\cdot}062$. Linolenic acid, although containing three double bonds, also obeys the second equation. G. GLASER

2760. **Estimation of oxalic acid by photochemical oxidation with ceric sulphate.** G. G. Rao and G. Aravamudan (*Z. anal. Chem.*, 1955, **145** [6], 426–430).—Ceric sulphate reacts only very slowly with oxalic acid in the dark at room temp. In the light, or at 50° C in the presence of a catalyst such as ICl or OsO_4, oxidation of the oxalic acid to CO_2 and H_2O is complete in 3 to 5 minutes. For the quant. determination of oxalic acid, the sample is mixed with an excess of standard $Ce_2(SO_4)_3$ soln., and exposed to bright sunlight or the light from a 1000-W tungsten-filament lamp for 15 min.; the excess of unchanged $Ce_2(SO_4)_3$ is titrated with standard Fe $(NH_4)_2SO_4$. The presence of high concn. of formic acid causes a slight (< 1 per cent.) positive error if sunlight is used, but there is no error with artificial light. Quartz or Pyrex-glass vessels may be used. A. R. ROGERS

2761. **Spectrophotometric determination of gluconic acid and its salts.** L. L. Alt (*Anal. Chem.*, 1955, **27** [5], 749–751).—A method is described for the determination of gluconic acid (**I**) which may be used even for highly alkaline soln. It is not specific for **I**, and other compounds (such as sugars) which form similar Cu complexes cause serious interference. *Procedure*—Treat the sample (containing 0·05 to 0·5 millimole of **I**) with 1·25 *M* NaOH (18 ml) and add 0·1 *M* aq. $CuSO_4$ soln. slowly from a burette, with stirring, until there is a permanent ppt. Boil for 5 min., cool to room temp. and pass through an ultra-fine sintered-glass filter. Wash the ppt. with 1·25 *M* NaOH (2 ml) and dilute the filtrate and washings to 50 ml with water. Measure the extinction at 660 mμ, with 0·5 *M* NaOH as blank. Beer's law is obeyed in the concn. range 10^{-3} to 10^{-2} *M*. The precision is $\simeq \pm 1{\cdot}5$ per cent. A. R. ROGERS

2762. **Characteristic chromatographic reactions for glucose and for acetone.** F. M. Shemyakin and O. S. Lobakhina (*Zh. Anal. Khim., SSSR*, 1955, **10** [1], 65–68).—The colour obtained in many reactions is made up of several different colours. The application of a chromatographic technique can enable a more definite identification to be made. A drop of glucose solution is placed on filter-paper, then in the same place a drop of copper citrate reagent followed by several drops of developer, *e.g.*, water, alcohol or acetone. After drying at 100° C for 3 min., a series of concentric rings of different colour and width are found, confirming the complexity of the colour. *Detection of glucose*—On paper place successively two drops of glucose solution, one drop of 10 per cent. NaOH solution and one drop of 1 per cent. $CuSO_4$ solution, and dry at 100° C. In the presence of glucose there appears a yellow - green spot with a pale-yellow ring, on the outside of which is a red - brown ring. In u.v., the spot is dark with first a violet ring and outside this a red - brown ring with pale blue on its periphery. *Detection of acetone with furfuraldehyde*—On paper place two drops of acetone solution containing a few μg per litre, then 1 drop of 1 per cent. furfuraldehyde soln. in 95 per cent. ethanol, and one drop of 10 per cent. NaOH solution. After drying, place one drop of conc. HCl in the centre of the spot; a red colour is given of intensity corresponding to the concn. of acetone and stable for 2 to 3 hr. In u.v., eight differently coloured rings appear. *Detection of acetone with sodium nitroprusside*—On paper place two drops of the acetone solution, one drop of 10 per cent. sodium nitroprusside solution and one drop of 10 per cent. NaOH solution. Then place a drop of glacial acetic acid in the centre of the red spot; a yellow spot with a pink ring is formed, which in u.v. appears grey with a blue ring. The method is suitable for detecting acetone in urine. G. S. SMITH

2763. **Source of error in infra-red determination of moisture in fluorocarbons.** F. J. Versagi (*Chemist Analyst*, 1955, **44** [2], 48–49).—When determining < 30 p.p.m. of H_2O in Freons (fluorocarbons), initially high absorbance readings are obtained owing to cooling caused by expansion of the fluorocarbon into the evacuated photometer cell. Greater accuracy is attained by leaving the sample in the cell for at least 3 min. before taking a reading; the precision is then 0·5 p.p.m. over the range 5 to 15 p.p.m. of H_2O. W. J. BAKER

2764. **Qualitative tests for some chloramine compounds.** E. J. Quinn and J. V. Karabinos (*Chemist Analyst*, 1955, **44** [2], 49–50).—Procedures are given for distinguishing between chloramine T

(sodium toluene-*p*-sulphonchloramide), Halane (1:3-dichloro-5:5-dimethylhydantoin), cyanuric chloride, trichloromelamine and chlorinated Na_3PO_4, when present in amounts of $\simeq$ 10 per cent. in built-up detergent mixtures containing Na_2CO_3, Na_2SiO_3 and sodium tripolyphosphate. Three tests involve treatment of separate and equal vol. of an alcoholic soln. of the sample with heat alone, catechol and 2:4-dinitrophenylhydrazine, respectively, whilst a fourth test is based on the reaction of $CuSO_4$ with an alkaline soln. of the sample. W. J. BAKER

2765. **Specific-surface determination of nitroguanidine by microscopic and air-permeability methods.** A. S. Bass and H. M. Sternberg (*Anal. Chem.*, 1955, **27** [5], 808–809).—Air-permeability equipment for the determination of the specific surface (S) of crystals shows very good precision, but accuracy is not claimed within $\pm$ 10 per cent. The S of acicular nitroguanidine crystals of irregular cross-section was determined microscopically by the introduction of cross-section area and perimeter-shape factors. The results with two pieces of air-permeability equipment were, respectively, 26 and 33 per cent. higher than the value determined microscopically. The authors regard the measurements as within a practical range of the true value, and recommend the equipment for the routine determination of S of acicular nitroguanidine crystals in the range 7000 to 9000 sq. cm per ml. A. R. ROGERS

2766. **Paper-chromatographic separation of 2-phosphoglyceric acid and 3-phosphoglyceric acid.** R. W. Cowgill (*Biochim. Biophys. Acta*, 1955, **16** [4], 614).—2-Phospho- and 3-phospho-glyceric acids can be separated on paper impregnated with molybdate salts. Whatman No. 52 paper is passed through 0·5 per cent. w/v $Na_2MoO_4.2H_2O$ solution and dried in air. Descending chromatograms are run with 88 to 90 per cent. formic acid - water - 95 per cent. ethanol (1:29:70) for 20 hr. at room temp. The spots are developed by a modification of the acid molybdate spray and u.v. light technique (Axelrod and Bandurski, *J. Biol. Chem.*, 1951, **193**, 405). G. W. CAMBRIDGE

2767. **The determination of organic substances. I. A new method for the estimation of potassium ethylxanthate.** Y. Arikawa (*Japan Analyst*, 1955, **4** [2], 91–94).—Potassium ethylxanthate is quant. pptd. with Ni^{++} in a neutral soln. The ppt. is dissolved in aq. NH_3 soln. and titrated with 0·01 *M* disodium ethylenediaminetetra-acetate, murexide being used as indicator. K_2CS_3, which is produced from KOH and excess of CS_2 on the conversion of an alcohol into K ethylxanthate, is decomposed to give K_2CO_3, CS_2 and CO_2 by passing CO_2 into a weakly basic soln. Hydrogen sulphide is driven off in a further current of CO_2 so that no NiS is produced on the addition of Ni^{++}. Potassium ethylxanthate remains unchanged during these procedures provided that the temp. is kept below 10° C. This method can be used for the determination of ethanol in dil. aq. soln., as shown below. **II. Determination of ethanol in a dilute aqueous solution.** (*Ibid.*, 1955, **4** [2], 94–99).—Experimental conditions for the quant. conversion of aqueous ethanol soln. ($<$ 1 per cent.) into K ethylxanthate with KOH and CS_2 were examined. When the sample ($<$ 5 ml) is treated with KOH (65 per cent.) (5 ml), CS_2 (1·2 ml) and dioxan (1 ml) (to increase the solubility of CS_2) at 40° to 45° C for 80 to 90 min., the yield of xanthate is not quant. but 72·9 $\pm$ 0·8 per cent. (empirical factor). The soln. containing K ethylxanthate, K_2CS_3 and excess of KOH is cooled below 10° C, partly neutralised with acetic acid and bubbled with a current of CO_2 for 40 min. The neutral soln. of K ethylxanthate thus obtained is treated with Ni acetate (5 mg of Ni per ml) (10 ml). The ppt. is dissolved in 2 *N* aq. NH_3 soln. and titrated with 0·01 *M* disodium ethylenediaminetetra-acetate, with murexide (0·25 mg) as indicator. No interference results from the presence of glycine ($<$ 5 mg per 5 ml), glucose ($<$ 10 mg) and hydroxycarboxylic acids. In the absence of other alcohols, methanol can be similarly determined. K. SAITO

2768. **Use of ultra-violet absorption spectra of saturated vapour mixtures for the determination of the chemical composition of the solution. Determination of naphthalene and tetralin in the presence of each other.** Gy. Versányi (*Acta Chim. Hung.*, 1955, **5** [3–4], 255–266).—The concentration of naphthalene (in solution with tetralin) was ascertained from the spectrum of the liquid mixture, that of tetralin from the spectrum of the vapour. The spectra were taken at 45° C and 60° C, with a cell length of 10 cm, by passing a light beam through the vapour in equilibrium with pure liquid tetralin or solid naphthalene. Since at these temp. liquid naphthalene can exist only in a supercooled state, its vapour pressure was determined by extrapolation of the vapour pressure - temperature curve. The values for naphthalene were corrected to allow for the continuous background caused by fluorescence. Data, obtained from six test samples, established a homogeneous continuous background over a range of 40 A. After determining the concentration of liquid naphthalene at 3105 A, the optical density of the solution was again measured at 3130 A and at 3090 A. The values, calculated from data for molar extinction coefficients at these points, differed only by $\simeq$ 0·05. The composition of the liquid was calculated from the values of vapour concentrations (based on the theory of regular solutions) by using Margules' equation for ternary systems (naphthalene, tetralin, sat. hydrocarbons). In the binary naphthalene - tetralin solutions the constant β of the activity coefficient was determined by direct measurement, the other β constants by means of analytical data collected from suitable synthetic mixtures. The average mol. wt. of the solution was estimated by comparing the concentrations of liquid and vapour. The max. relative error was found to be 5 per cent. for naphthalene and 10 per cent. for tetralin determinations. The concentration of benzene, toluene and monomethylnaphthalenes in the presence of naphthalene and tetralin can be ascertained by the same method; xylenes, however, interfere. S.C.I. ABSTR.

2769. **Detection of unsubstituted *para*-position in phenols.** S. Soloway and A. Santoro (*Anal. Chem.*, 1955, **27** [5], 798–800).—Phenols are readily oxidised to coloured products in ammoniacal soln. by the persulphate ion in the presence of a catalytic amount of Ag^+. Derivatives having a free *p*-position are distinguished from others in yielding blue or green dyes, which are pH and redox indicators; comparison of absorption spectra after purification by chromatography on Al_2O_3 suggests that they may be indophenol derivatives. With phenols containing electro-negative groups in the *o*- or *m*-positions, preliminary hydrolysis and reduction must be carried out. *Procedure*—Dissolve the phenol (10 to 20 mg) in 2 *M* NaOH (1 ml), reflux for 5 min. with zinc dust (50 mg), centrifuge, decant, and to the supernatant liquid add 2 *M* $AgNO_3$ (2 drops) and

$K_2S_2O_8$ (10 to 20 mg). Compounds containing unsubstituted *p*-positions yield a green, blue - green or blue colour within 15 sec.; otherwise a yellow, orange or amber colour results. Heat with zinc dust (30 mg), centrifuge and decant; the supernatant liquid should become paler or colourless, but re-oxidises to the earlier colour on being shaken with air. Some *p*-halogenated phenols give a positive test; this is attributed to migration of the halogen group in the course of the reaction.

A. R. ROGERS

2770. **Coulometric titration of salicylic acid.** B. Kawamura, K. Momoki and S. Suzuki (*Japan Analyst*, 1954, **3** [1], 29–32).—A rapid determination of a micro-amount of salicylic acid by coulometric titration was studied by the use of Br and Cu^I produced through electrolysis. Since the bromination of salicylic acid is slow, an excess of Br is generated and titrated with Cu^I coulometrically. The sample (50 to 300 μg) is dissolved in an electrolyte composed of 0·3 *N* HCl, 0·1 *N* $CuSO_4$ and 0·1 *M* KBr, and the time of electrolysis is measured at a constant current of 10 mA. A potential difference of 250 mV is applied between the indicator electrodes, and the end-point is observed amperometrically. K. SAITO

2771. **The volumetric determination of thiobenzophenone and xanthione.** R. C. Moreau (*Bull. Soc. Chim. France*, 1955, **4**, 569–571).—The reaction between silver nitrate and aromatic thioketones in 95 per cent. ethanol has been studied and used to determine thiobenzophenone in an impure sample. The reaction is shown to be in accord with theory. A red unstable complex is formed and immediately decomposes to give benzophenone and a precipitate of silver sulphide, which can be filtered off. The excess of silver nitrate can then be titrated in the usual way. The presence of elementary sulphur gives no significant error under the given conditions. Recoveries of 99 to 101·3 per cent. are given with pure xanthione. *Procedure*—Boil a suitable quantity of the thioketone in 10 ml of 95 per cent. ethanol. To the warm solution add 10 ml of 0·2 *N* $AgNO_3$ in 95 per cent. ethanol. Shake, set aside for 5 to 10 min. and dilute to 100 ml with water. Filter and titrate the excess of $AgNO_3$ in 50 ml of filtrate with 0·1 *N* NH_4SCN. K. A. PROCTOR

2772. **Colour reaction for determination of some aromatic nitro compounds.** C. C. Porter (*Anal. Chem.*, 1955, **27** [5], 805–807).—Certain mononitro compounds (5 to 100 μg), mainly deriv. of *o*- and *p*-nitroaniline and of *p*-nitrotoluene, develop orange, red or purple colours in dimethylformamide (9·9 ml) with 10 per cent. aq. tetraethylammonium hydroxide (0·1 ml). The colours developed by this reaction, and also by the NaOH - acetone (Janovsky) reaction, together with values of $\lambda_{max.}$ and $E_{max.}$, are tabulated for 67 aromatic nitro compounds. A number of the substances examined gave colours of sufficient stability to permit the construction of standard curves, which should provide a basis for quant. determination. A. R. ROGERS

2773. **Quantitative analysis by infra-red spectroscopy. III. Quantitative analysis of isomers of dinitronaphthalene in the dispersed phase in liquid paraffin.** H. Kamada and S. Tanaka (*Japan Analyst*, 1955, **4** [2], 71–73).—The determination of 1:5-dinitronaphthalene (**I**) and 1:8-dinitronaphthalene (**II**) (both insol. in CS_2 or CCl_4) in the binary mixture was studied by means of infra-red spectra in liquid paraffin (max. absorption, 11·24 μ for **I**, 11·96 μ for **II**). When the molar ratio of **I** to **II** is plotted against the ratio $B/(B - A)$ (A is the extinction of the mixture at 11·24 μ and B at 11·96 μ), a linear working curve is obtained, which is independent of the thickness of the layer of the suspension. 1-Nitronaphthalene should be removed by extracting with CS_2. An attempt was made to make the light scattering constant and the thickness of the layer uniform. The average deviation from the mean is $< \pm 2$ per cent. within the range 30 to 50 per cent. of **I**. K. SAITO

2774. **Polarographic determination of *cyclo*hexyldinitrophenols, especially of 6-*cyclo*hexyl-2:4-dinitrophenol.** M. Maruyama and K. Maruyama (*Japan Analyst*, 1954, **3** [1], 11–16).—The polarographic determination of 6-*cyclo*hexyl-2:4-dinitrophenol (**I**) in the binary mixture with 6-*cyclo*hexyl-2:6-dinitrophenol (**II**) was studied in 50 per cent. ethanolic soln. containing KCl (0·1 *M*) as supporting electrolyte. The change of $E_{\frac{1}{2}}$ of both isomers was examined at various pH values. At pH 7, **II** shows one reduction wave ($E_{\frac{1}{2}}$ — 0·63 V *vs.* the N.C.E.), whilst **I** shows two waves (— 0·54 and — 0·91 V), the second being in accord with Ilkovič's equation within the range 0·02 to 0·12 mg of **I** per ml. The influence of temp., concn. of ethanol, concn. of gelatin and the passage of N was examined and sources of error are discussed. The average deviation from the mean is $\simeq 2$ per cent. for samples containing $\simeq 85$ per cent. of **I**. The results for industrial products agree with those obtained by the infra-red absorption method. *Procedure*—The sample ($\simeq 50$ mg) is dissolved in 50·0 ml of ethanol. One ml of the soln. is diluted with 4 ml of ethanol and 5 ml of buffer, pH 7, containing KCl (0·1 *M*) and gelatin (5 g per litre of the buffer soln.) and submitted to polarography at 25° C. K. SAITO

2775. **Chromatographic separation of 2:4-dinitrophenylhydrazones.** J. A. Elvidge and M. Whalley (*Chem. & Ind.*, 1955, [21], 589–591).—A mixture of bentonite and kieselguhr (4:1) is a satisfactory adsorbent for rapid and near-quant. separation of mixtures of the dinitrophenylhydrazones of the lower aldehydes and ketones. Carbon tetrachloride, benzene and chloroform, and their mixtures with ethanol, are recommended as eluting solvents. The mixed adsorbent should be packed into the column as a thickish slurry with the solvent. Details of a series of separations carried out by this method are tabulated. S.C.I. ABSTR.

2776. **Order of adsorption affinities of polynitrostilbenes.** A. F. Teague, W. A. Gey and R. W. Van Dolah (*Anal. Chem.*, 1955, **27** [5], 785–786).—The relative adsorption affinities of a series of polynitrostilbenes have been evaluated for two adsorbents, with a mixture of benzene and Skellysolve B as solvent. With a 3:1 mixture of silicic acid and Celite 535 as adsorbent, adsorbability varies as expected, increasing with the number of nitro groups. With a 5:3 mixture of kaolin and Celite 535, the order is almost completely reversed. No explanation is offered. A. R. ROGERS

2777. **Estimation of phenolic substances: use of stabilised *p*-aminodiethylaniline.** B. Camber (*Nature*, 1955, **175**, 1085).—Salicyloylhydrazones (*cf. Anal. Abstr.*, 1955, **2**, 2614) were estimated as follows. To 5 to 50 μg of the salicyloylhydrazone dissolved in 1 ml of ethyl acetate was added 1 ml of 0·1 per cent. solution of *p*-aminodiethylaniline (stabilised with SO_2). Aqueous 5 per cent. $NaHCO_3$ soln. (1 ml) was added, followed by 2 ml of a saturated aq. KIO_4 soln. The reaction mixture was then shaken

thoroughly during the formation of the indoaniline. Water (3 ml) and powdered NaCl were then added followed by the required amount of ethyl acetate. A crystal-clear intensely coloured supernatant organic phase resulted, which was decanted and read in a Spekker colorimeter against a blank determination, a suitable filter being used. The use of $K_3Fe(CN)_6$ as an oxidant is illustrated by the following method for the estimation of phenols. To 1 to 10 μg of phenol dissolved in 1 ml of water were added 0·4 ml of 0·1 per cent. stabilised *p*-aminodiethylaniline, 0·5 ml of 0·33 per cent. $K_3Fe(CN)_6$ soln. and 0·5 ml of 5 per cent. potassium pyroborate, and the intensity of the colour was read directly. For the estimation of < 1 μg of phenol, the indoaniline should be extracted into *n*-butanol or chloroform. If necessary, this extract may be concentrated by distillation. Other effective oxidants are $AgNO_3$ and $HgCl_2$. The reaction appears to be general for phenolic substances.

O. M. WHITTON

2778. **Correlation between equilibrium flash vaporisation and A.S.T.M. distillation data of petroleum mixtures.** J. C. Chu and E. J. Staffel (*J. Inst. Petrol.*, 1955, **41** [375], 92–99).—Existing correlations are examined and a method which is a modification of that of Edminster and Pollock (*Chem. Engng Progr.*, 1948, **44**, 905) is developed.

G. SKIRROW

2779. **Analysis of automobile exhaust-gases by mass spectrometry.** J. K. Walker and C. L. O'Hara (*Anal. Chem.*, 1955, **27** [5], 825–828).—The greatest problem in automobile exhaust-gas analysis is that of representative sampling. By continuous recording of mass spectra at various engine speeds, the authors have demonstrated changes in exhaust-gas composition with speed. At high engine speeds the hydrocarbon and air contents approach a steady state, whereas the oxides of nitrogen increase proportionately with speed and temperature.

K. A. PROCTOR

2780. **Determination of the pitch content of coal-tar briquettes.** W. Winzen (*BrennstChemie*, 1955, **36** [5–6], 85–87).—The standard method of determining pitch in briquettes, by continuous extraction with CS_2 in a Soxhlet thimble, is slow, and there is a continuous creep of fine insoluble particles through the thimble and over the top. Constant results can be obtained after 1 hour's extraction if the thimble and siphon are replaced by a double or treble fluted paper, in a funnel shaped like a Gooch adapter, draining into another fine fluted paper in a hemispherical funnel with a siphon at the base. The condenser is so designed, with a tap at the bottom, that the solvent can be evaporated from the extracted pitch without dismantling the apparatus.

A. B. DENSHAM

2781. **Hydrosulphite [dithionite] analysis with special regard to control of vat dyebaths.** A. Airoldi and F. Marchi (*Amer. Dyest. Rep.*, 1955, **44**, 283–288).—The various methods of estimating dithionite are reviewed and discussed, and a control method is evolved for the rapid determination of the amount present in a vat dyebath. The sample is added, by pipette, under the surface of a mixture of formaldehyde, acetic acid and NaCl soln. contained in a calibrated flask. The mixture is made up to 100 ml and set aside for 2 min. It is then shaken until homogeneous, and filtered, and an aliquot of the filtrate is titrated with 0·1 *N* iodine soln. (starch indicator). The end-point is indicated by a blue colour persisting for 10 to 15 sec. The quantities recommended are: 20 to 30 ml of formaldehyde (36 to 40 per cent.), 10 to 15 ml of 10 per cent. acetic acid (to give the required pH), $\simeq 2$ g of NaCl, and a 50-ml sample from the dyebath. A 50-ml aliquot of the filtrate is used for the titration. 1 ml of 0·1 *N* iodine soln. $\equiv$ 0·004353 g of $Na_2S_2O_4$.

S.C.I. ABSTR.

2782. **I.W.T.O. [International Wool Textile Organisation] method for the determination of the ether-soluble extract of wool tops.** Anon. (*J. Text. Inst. Manchr Proc.*, 1955, **46** [3], s45–46).—Weighed conditioned wool (20 g) is placed in an all-glass Soxhlet extractor (capacity 200 to 300 ml), and extracted with anhydrous ether (peroxide- and ethanol-free), under conditions which are laid down in detail in the specification.

L. VALENTINE

2783. **Studies on the determination of the ether-soluble extract of wool carried out by the Technical Committee of the I.W.T.O.** M. Robinet (*J. Text. Inst. Manchr Proc.*, 1955, **46** [3], s47–50).—Previous attempts to obtain reproducible results for the ether-soluble fraction of wool tops are described, and a refined technique of sampling tops is presented. With the standard technique described previously (*Anal. Abstr.*, 1955, **2**, 2782), two analysts in each of six different laboratories analysed a varying number (3 to 7) of samples from the same bulk of wool top. In all, 68 determinations were made with the following results expressed as mg of extract from 20 g of wool; over-all mean 94·6, range 26, standard deviation $\pm$ 6·05.

L. VALENTINE

2784. **Rapid determination of ash in paper.** D. F. Petersen (*Chemist Analyst*, 1955, **44** [2], 46–47).—A procedure, occupying only $\simeq 5$ min., for routine determinations of ash in paper, involves accelerated combustion of the air-dry sample (3 to 4 g) in a nickel crucible (65 to 70 ml) in a preheated furnace by means of a gentle stream of oxygen projected across the top of the crucible during ignition ($\simeq 1$ min.). The oxygen is supplied from a "lance" constructed from metal tubing that connects with the outlet of the cylinder. The tare of the crucible should be periodically checked.

W. J. BAKER

2785. **Analysis of cellulose acetate butyrate.** N. R. Kamath and S. Sourirajan (*Paintindia*, 1955, **5** [1], 77–81).—The sap. val. is determined by dissolving the sample (1 g) in acetone (25 ml), adding 1 *N* alcoholic KOH (25 ml), refluxing for 1 hr., cooling, adding 0·5 *N* aq. HCl (50 ml), shaking, allowing to stand for 10 min., then titrating with 0·1 *N* alcoholic KOH. A blank determination is carried out. The hydroxyl value is determined by dissolving the sample (1 g) in pyridine (25 ml), adding acetylating reagent (acetic anhydride - H_2O - pyridine, 20:0·35:100, by vol.) (10 ml), refluxing, cooling, adding ice-cold H_2O (20 to 30 ml) followed by nitrobenzene (20 ml), keeping in crushed ice for 30 min., and titrating with 0·5*N* alcoholic KOH (thymolphthalein); a blank determination is made. From the sap. value and hydroxyl value the acetyl and butyryl contents may be calculated. If plasticisers are present, they must first be removed by exhaustive extraction with hexane.

L. A. O'NEILL

2786. **Detection of surface-active agents containing polyoxyethylene or polyoxypropylene group by pyrolysis with phosphoric acid.** M. J. Rosen (*Anal. Chem.*, 1955, **27** [5], 787–790).—The present

qual. tests for the polyoxyethylene group are non-specific. A method is proposed based on pyrolysis of the sample (200 mg) in the presence of 85 per cent. H_3PO_4 (1 to 1·5 ml) to yield acetaldehyde, which gives a blue colour with a soln. of diethanolamine (1 drop) and sodium nitroprusside (2 drops of a 4 per cent. soln. in 90 per cent. methanol) in water (1 ml). Under the same conditions, the polyoxypropylene group yields propionaldehyde, which gives an orange colour. If both groups are present, an orange colour is given which quickly turns brown. Positive results have been obtained with all tested surface-active compounds (37) containing these groups, and negative results with all others (15). The only compounds that yield positive results in the absence of these groups are glycerides, which decompose in the test to acraldehyde (giving a blue colour). A. R. ROGERS

2787. **New specific determination of thioglycollic acids [in cold-wave solutions].** D. von Keller (*Seifen-Öle-Fette-Wachse*, 1954, **80**, 560).—The formation of a colourless complex between a copper salt and thioglycollic acid (**I**) can be used to determine **I**. The soln. of copper salt is prepared by mixing 57·5 g of $CuSO_4.5H_2O$, 500 g of H_2O and about 60 g of 2-aminoethanol (free from Fe), shaking or stirring until the $Cu(OH)_2$ has redissolved and adding H_2O to 1 litre. To determine **I** in a cold-wave soln., 5 ml are made alkaline with aq. NH_3 (if not already present) and titrated with the alkaline Cu soln. until a stable yellow colour appears. The no. of ml consumed indicates the percentage of **I** in the cold-wave soln. The method gives accurate results with **I** soln. containing NH_3 alone or with $(NH_4)_2SO_3$ or $Na_2S_2O_4$. CHEM. ABSTR.

2788. **Acid value of rosin derivatives.** N. R. Kamath and G. D. Shetye (*Paintindia*, 1955, **5** [1], 73–76).—Rosin derivatives (treated rosins, rosin esters, or rosin-modified phenolic resins) other than maleic resins are dissolved in toluene (25 ml), ethanol (2·5 ml) is added and the mixture is titrated against 0·1 *N* ethanolic KOH with the use of bromothymol blue. For maleic resins, absolute methanol is used in place of ethanol, and titration is carried out against 0·05 *N* methanolic Na methoxide. L. A. O'NEILL

2789. **Aminolysis as an aid in the chemical analysis of synthetic resins.** C. P. A. Kappelmeier (*Fette u. Seifen*, 1955, **57** [4], 229–230).—When a mixture containing urea resins is boiled with benzylamine or with 2-phenylethylamine, the urea resins are quant. converted into symmetrical disubstituted ureas, which can be identified by their m.p. The amount of urea resin present in the mixture is calculated from the weight of derivative obtained. On being warmed with 2-phenylethylamine, alkyd resins yield the corresponding amides of the fatty and dicarboxylic acids, together with the polyalcohols present. In this way, glycerol and pentaerythritol are separated from a phthalate resin based on pentaerythritol and linseed oil. E. HAYES

2790. **Analysis and testing [of liquid paints].** Anon. (*Paint Manuf.*, 1955, **25** [1], 28–30).—Recently developed methods of chemical analysis, including absorption spectrometry, isotopic, chromatographic and polarographic techniques, and physical testing methods, are reviewed. (32 references.) D. R. DUNCAN

2791. **Determination of weak acids and their salts in some vegetable tan liquors.** P. H. Rao and B. S. Srikantan (*J. Indian Chem. Soc., Ind. Ed.*, 1954, **17**, 229–235).—Atkin and Burton's method (*J. Int. Soc. Leath. Chem.*, 1949, **33**, 52) of calculating weak acids in tan liquors is modified to allow for variations in buffer index. Potentiometric titrations were conducted with the extracts, and graphs of pH *vs.* vol. of titre (v), and ($\triangle$pH/$\triangle v$) *vs.* vol. of titre were drawn. In the latter graphs, sharp maxima were obtained corresponding to individual weak acids or salts in the extracts. The small buffer regions depicted by the troughs are eliminated, and each acid is calculated separately. Total acids are found by addition. Similar calculations are made for salts. A. M. SPRATT

2792. **The estimation of chromium in hides.** J. R. Rossi (*Chim. Anal.*, 1955, **37** [5], 161–162).—An alternative to the official method for the estimation of Cr in hides is proposed. Greater accuracy, as a result of easier manipulation, is claimed. *Procedure*—Transfer about 1 g of sample, accurately weighed, into a 300-ml Kjeldahl flask and add a mixture (1 + 1)(15 ml) of 50 per cent. HNO_3 and 50 per cent. H_2SO_4. After the first vigorous reaction heat for 10 min., cool and add 5 ml of H_2O_2 soln. (110 vol.). Boil gently and heat to fuming. Repeat the addition of H_2O_2 if necessary. Cool and dilute. Add 5 ml of $AgNO_3$ soln. (2 per cent.) and 10 ml of ammonium persulphate soln. (40 per cent.), and boil for 30 min. Precipitate the excess of Ag^+ with HCl (10 ml), filter and determine the oxidised Cr in the filtrate by titration of iodine liberated from 10 ml of KI soln. (10 per cent.) with 0·1 *N* $Na_2S_2O_3$ soln. D. G. FORBES

See also Abstracts 2616, 2622, 2872, 2873, 2874.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

2793. **Photometric determination of sodium in blood-serum with violuric acid.** R. F. Muraca and J. P. Bonsack (*Chemist Analyst*, 1955, **44** [2], 38–42).—The photometric procedure described and discussed depends on the differing colours and solubilities of alkali and alkaline-earth violurates in anhyd. dimethylformamide. W. J. BAKER

2794. **A colorimetric method for the estimation of serum magnesium.** A. J. Smith (*Biochem. J.*, 1955, **60** [3], 522–527).—Methods for the determination of Mg are discussed. A colorimetric method is described for the determination of Mg in serum with an accuracy of $\pm$ 5 per cent. The method depends on the use of a soluble coloured complex of Mg with Eriochrome black T and measurement of the colour spectrophotometrically. After removal of Ca as oxalate, the supernatant fluid is deproteinised with trichloroacetic acid, and the filtrate is subjected to spectrophotometry. A calibration is made in parallel with each batch of analyses, on a control on reagents and a set of standards treated with the reagents to correspond with the serum filtrate. The results for control and standard are plotted and the unknowns are read from the graph. J. N. ASHLEY

2795. **The direct micro-determination of calcium in urine by nephelometry.** G. S. Stewart, H. F. Bowen and E. M. Cullerton (*J. Lab. Clin. Med.*, 1955, **45** [4], 653–657).—The rapid method described

requires 0·1 ml or less of sample and is based on the formation of a stabilised suspension of Ca oleate in aq. NH_3 soln. No statistically significant difference was found between results by the proposed method and those given by methods which require ignition and wet-oxidation followed by pptn. as Ca oxalate. Calibration is rectilinear with 5 to 20 μg of Ca. *Reagents*—(*i*) Shake 16·5 ml of oleic acid with 10 ml of water containing 3·2 g of KOH. Transfer the emulsion to a flask with the aid of 100 ml of 70 per cent. ethanol, reflux for 1 hr. and dilute to 500 ml with water. (*ii*) 10 per cent. aq. sodium lauryl sulphate (Duponol). (*iii*) Mix 5 vol. of (*i*) with 2 vol. of (*ii*). Filter before use. (*iv*) Dilute 37 ml of conc. aq. NH_3 to 100 ml with water. (*v*) Calcium standard. Carefully dissolve 250·2 mg of Iceland spar ($CaCO_3$) in 10 ml of conc. HCl and dilute to 100 ml with water. Dilute 1 ml to 100 ml with water (1 ml ≡ 10 μg of Ca). *Procedure*—Add 1 ml of conc. HCl to each 100 ml of sample and filter a portion of the mixture through a sintered-glass filter. Transfer 0·1 ml of the filtered sample by pipette into a nephelometer cell containing 4·5 ml of water. Add 3 drops of (*iv*) and mix. Add 0·4 ml of (*iii*) and immediately mix thoroughly. Read the turbidity produced after 30 min. against similarly prepared standards containing 10 μg of Ca in the same final vol. Also prepare a reagent blank. Calculate the calcium content of the test solution from the formula of the regression line established previously from the standard curve for the particular instrument. A Coleman Model 9 Nephocolorimeter with Polaroid filter was found suitable.
W. H. C. SHAW

2796. **Improved methods of analysis for oxygen, carbon monoxide and iron on finger-tip blood.** S. Natelson and C. M. Menning (*Clin. Chem.*, 1955, **1** [3], 165–179).—Oxygen and CO are estimated by conventional gasometric methods on a micro scale with an improved micro-gasometer. Iron is estimated as thiocyanate after wet-ashing 0·02 ml of whole blood or 0·5 ml of serum or plasma with H_2SO_4 and $HClO_4$. H. F. W. KIRKPATRICK

2797. **A sensitive method for the estimation of hydrogen peroxide in biological materials.** W. A. Andreae (*Nature*, 1955, **175**, 859–860).—The intensity of fluorescence of scopoletin (7-hydroxy-6-methylcoumarin) (**I**) is proportional to concn. up to $2·5 \times 10^{-6}$ *M* in borate buffer of pH 10. One mole of H_2O_2 is required for the oxidation of one mole of **I**, and so **I** may be used as a fluorescent indicator for the peroxidative estimation of H_2O_2. After the removal of interfering reducing substances (*e.g.*, ascorbic acid, glutathione, Mn^{++}) by oxidation, approx. 10^{-10} mole amounts of endogenously produced H_2O_2 can be determined quant. by adding a known amount (excess) of **I** and a source of peroxidase, allowing to stand for a few minutes, diluting with buffer and measuring the residual fluorescence. This represents a 100-fold increase in sensitivity over previous methods.
A. R. ROGERS

2798. **Assay of iron-55 and iron-59 in biological samples.** J. H. Rediske, R. F. Palmer and J. F. Cline (*Anal. Chem.*, 1955, **27** [5], 849–850).—A rapid sensitive method is described for detecting ^{55}Fe and ^{59}Fe, either individually or in mixed preparations, which is suitable for the analysis of plant tissue. The sample is digested with H_2SO_4 and $HClO_4$, and the Fe is extracted as the ferric thiocyanate complex with a 1:1 mixture of ether and *iso*amyl alcohol. An aliquot of the organic phase is evaporated on a stainless-steel counting plate to an "infinitely thin" sample, and the activity is determined in a windowless methane-flow proportional counter. Counts are made with and without a rubber hydrochloride absorber (0·625 mg per sq. cm), which reduces the ^{55}Fe count to 1·5 per cent. and the ^{59}Fe count to 66 per cent. A. R. ROGERS

2799. **Studies on the inorganic constituents in biological materials. III. The simultaneous spectrochemical analysis of inorganic constituents with a logarithmic sector.** N. Ohta and Y. Tomita (*Japan Analyst*, 1954, **3** [1], 22–25).—The simultaneous determination of Na, K, Ca, Mg, Fe, Mn, Sr, Ba, Zn, Al and B in animal organs was studied by means of an arc spectrographic method, with Ni^{++} as internal standard. The sample (1 g) is decomposed with fuming HNO_3 and 30 per cent. H_2O_2; Ni^{++} (30 mg per ml) (1 ml) are added and the soln. is evaporated to dryness with 6 *N* HCl. The residue is placed on a copper rod and burnt in a d.c. arc (150 V, 4 A, exposure 1 min.). The light is introduced into a spectrograph (Zeiss, Qu24) through a logarithmic sector. The length of the spectral lines is measured on the photographic plate and compared with that of Ni 3002·49 A (for Mg, B and Na) or Ni 3858·3 A (for the remaining elements). In a normal organ, Na, K, Mg, Ca and Fe can be determined satisfactorily, but the emission spectra of the other elements are not intense enough for measurement, unless there is an abnormal concn. in the organ. K. SAITO

2800. **Colorimetric determination of the ethanol content of blood.** E. Pfeil and H.-J. Goldbach (*Klin. Wochschr.*, 1955, **33** [21–22], 536).—The Widmark method is modified so that excess of dichromate after oxidation of ethanol is determined colorimetrically. The oxidation is carried out at 55° C for 2 hr. to avoid the error due to acetone; the reaction mixture is then washed into a 1-litre calibrated flask with water to about 500 ml, 3 ml of conc. H_2SO_4 and 5 ml of a 2 per cent. soln. of diphenylcarbazide in acetone are added, and the soln. is made up to the mark with water. The extinction is read at 550 mμ in a 1-cm cell; the value obtained, subtracted from that given by the blank, gives a measure of the dichromate used in the oxidation of the ethanol. H. F. W. KIRKPATRICK

2801. **Detection of alcohols in cadaver blood.** W. Schwerd (*Dtsch. Z. ges. gerichtl. Med.*, 1954, **43**, 221–231).—The formation of volatile reducing substances in putrifying blood was followed by the Widmark method and by Wenig's distillation method (**I**). Alcohols by **I** reached 0·048 per cent. in human blood in contact with air and over 0·1 per cent. in the absence of air. In cadavers, several months after death, values by **I** were about 0·1 per cent. Ethanol was 50 to 95 per cent. of the total, with smaller amounts of propanol to pentanol, and traces of methanol. The nitrobenzaldehyde reaction was used to test for higher alcohols. Up to 4 days after death there is no interference from alcohol formation. In blood taken from cadavers, alcohol formation can be prevented by addition of 1 per cent. of NaF. CHEM. ABSTR.

2802. **Possible errors in volumetric measurement in the determination of blood ethanol.** F. Portheine and H. Zimmermann (*Z. anal. Chem.*, 1955, **145** [4], 241–245).—Errors arising in the determination of blood ethanol due to the use of the normal clinical pipette are discussed. A pipette with a shorter

measuring length, which allows serum and blood, water or ethanol to be measured with an accuracy of ± 0·1 mg, is described. R. J. MAGEE

2803. **The estimation of pyruvic acid in human serum.** B. Hess (*Klin. Wochschr.*, 1955, **33** [21–22], 540–541).—In a previous paper (*Anal. Abstr.*, 1955, **2**, 1283) lactic acid dehydrogenase was proved to exist in human serum. The presence of this enzyme coupled with addition of reduced diphosphopyridine nucleotide (DPN) provides a simple means of determining pyruvic acid according to the reaction pyruvic acid + reduced DPN ⇌ lactic acid + oxidised DPN. Serum (1 ml) is mixed with 1·5 ml of tri(hydroxymethyl)methylamine buffer, pH 7·4, and 0·04 ml of reduced DPN (0·3 μM), and the reaction is followed in a spectrophotometer at 340 or 366 mμ. The reaction continues for about 10 to 20 min. at room temp., but proceeds rapidly at higher temp. or after addition of cryst. lactic acid dehydrogenase. Addition of the enzyme may be necessary in severe pathological cases. The test is vitiated by haemolysis. Normal sera were found to contain about 400 μg per cent. of pyruvic acid by this method. H. F. W. KIRKPATRICK

2804. **A colorimetric method for the quantitative determination of phenylpyruvic acid in urine.** K. Kropp and K. Lang (*Klin. Wochschr.*, 1955, **33** [19–20], 482–485).—The accepted test for phenylpyruvic acid, namely production of a green colour on addition of $FeCl_3$ to the acidified soln., is unsuitable for quant. determination owing to the rapid fading of the colour. If $FeCl_3$ is replaced by ferric citrate, a sufficiently stable colour is produced to permit measurement of the extinction. The method recommended is as follows. Urine (4 ml, diluted 1:20) are acidified with 1 ml of 1 per cent. citric acid and treated with 1 ml of 10 per cent. ferric citrate. During the interval between the 3rd and 7th min. after the mixture has been made, the extinction is measured at 620 mμ through a 2-cm layer of the soln.; a comparison tube is prepared as described, 4 ml of water being used in place of the urine. Owing to the 1:20 dilution, the colour of the urine can be ignored. The concn. (c) of the phenylpyruvic acid in mg per 100 ml can be determined by reference to a calibration curve (reproduced in the text) or by calculation from the equation $c = F \times E$ in which E is the extinction and F is a factor 263·2. The calibration curve is not reliable for 100 to 150 mg per 100 ml and if the concn. exceeds this value the urine must be diluted still more. Acidification is necessary to prevent pptn. of iron by phosphates, etc. The method cannot be used if the urine contains even traces of protein nor if patients have taken pyrazolone drugs. P. HAAS

2805. **Plasma creatinine.** M. Ralston (*J. Clin. Pathol.*, 1955, **8** [2], 160–162).—The use of Lloyd's reagent for adsorption of creatinine from plasma (*Biochem. J.*, 1954, **58**, 426) has been investigated for specificity by chromatography of the adsorbed material. Eluates showed only one Jaffé-positive spot identical with that of creatinine, and the method is concluded to be specific for creatinine. The ceric sulphate oxidation method (*Biochim. Biophys. Acta*, 1952, **8**, 86) was also investigated and was found not to eliminate entirely non-specific Jaffé-positive substances. H. F. W. KIRKPATRICK

2806. **A spot test for serum bilirubin.** A. W. Farmer (*J. Med. Lab. Technol.*, 1955, **13** [1], 24–25).—This is an emergency procedure which can be carried out in a few minutes with 1 drop of serum by the use of diazotised sulphanilic acid and comparing the colour produced with standards. F. W. DIGGINS

2807. **An assessment of new tests for detecting bilirubin in urine.** D. Bryant and F. V. Flynn (*J. Clin. Pathol.*, 1955, **8** [2], 163–165).—A tablet test has been compared with two forms of the Fouchet test and with the iodine test. The only unsatisfactory test is the iodine test, which should be replaced by one or other of the others. H. F. W. KIRKPATRICK

2808. **A chromatographic method for the determination of the three bile pigments in serum.** B. H. Billing (*J. Clin. Pathol.*, 1955, **8** [2], 126–129).—Bilirubin, pigment I and pigment II (*Biochem. J.*, 1954, **57**, 514) are separated on a silicone-treated kieselguhr column and estimated by converting into the azo compounds, as in the Van den Bergh test. It was found that the sum of the values obtained for pigments I and II was not significantly different from the value for "direct bilirubin" given by the method of Malloy and Evelyn (*J. Biol. Chem.*, 1937, **119**, 481). The "1 minute" bilirubin of Ducci and Watson (*J. Lab. Clin. Med.*, 1945, **30**, 293) is more closely related to the total amount of direct-reacting pigment than to a particular pigment. H. F. W. KIRKPATRICK

2809. **Chromatographic separation and determination of porphyrin methyl esters.** D. A. Rappoport, C. R. Calvert, R. F. Loeffler and J. H. Gast (*Anal. Chem.*, 1955, **27** [5], 820–822).—The methyl esters of uroporphyrin I, coproporphyrins I and II, and protoporphyrin IX may be separated within one hour by horizontal chromatography on filter-paper placed between glass plates. Elution of individual bands from the paper chromatogram with 1·5 N HCl, followed by fluorimetric analysis, permits estimation of each porphyrin ester with an accuracy within ± 3 per cent. and a sensitivity ≃ 0·1 μg. *Procedure*—Esterify the mixed porphyrins in the crude extract by standing overnight at room temp. in the dark with 3 to 4 volumes of methanol saturated with HCl gas. Add water (5 vol.) and extract into $CHCl_3$. Separate the $CHCl_3$ phase, wash with 10 per cent. sodium acetate soln., then with water, and concentrate to about 1 ml in a vacuum desiccator. Apply approx. 0·1 ml to the centre of a 13-in. square of Whatman No. 3 MM filter-paper, allow to dry, and clamp between horizontal glass plates. Develop successively with 2 ml of a 3:1 mixture of light petroleum (boiling range 30° to 60° C) and $CHCl_3$, and with 8 ml of a 40:2:3 mixture of heptane - ethylene dichloride - *tert.*-butanol. If the sample contains large amounts of impurities, a preliminary development with 2 ml of a 1:1 mixture of light petroleum - $CHCl_3$ is desirable; the impurities will remain at the origin. A. R. ROGERS

2810. **Indirect analysis of corticosteroids. I. The determination of 17-hydroxycorticosteroids.** J. I. Appleby, G. Gibson, J. K. Norymberski and R. D. Stubbs (*Biochem. J.*, 1955, **60** [3], 453–460).—A combination of reductive and oxidative procedures is used in a method for the determination of urinary total 17-hydroxycorticosteroids; it depends on their conversion into 17-ketosteroids in the urine and measurement of these as chromogens in the Zimmermann reaction. The analytical sample is reduced by $NaBH_4$ under conditions that ensure quant. conversion of ketones into alcohols, and is subsequently oxidised with sodium bismuthate. During reduction the 17:20-ketols are converted

into the corresponding 17:20-glycols; these, whether thus formed, or originally present, are degraded into 17-ketones during oxidation. This sequence of reactions converts all 17-hydroxycorticosteroids into 17-ketosteroids; all other ketones originally present, including 17-ketosteroids, are reduced to alcohols. The method, which has increased accuracy, is rapidly performed, and one person can assay (in duplicate) twelve urines in one day.

J. N. ASHLEY

2811. **Indirect analysis of corticosteroids. II. The determination and identification of urinary 17-hydroxy-20-ketosteroids unsubstituted at $C_{(21)}$.** J. I. Appleby and J. K. Norymberski (*Biochem. J.*, 1955, **60** [3], 460–467).—A method is described for the group determination of 17-hydroxy-20-ketosteroids, unsubstituted at $C_{(21)}$, by their selective conversion into 17-ketosteroids and measurement of these as chromogens in the Zimmermann reaction. The determination is made on an extract of urine that has been hydrolysed with 10 per cent. aq. HCl. The extract is treated with sodium bismuthate, which converts all 17-hydroxycorticosteroids, other than 21-deoxyketols, into 17-ketones; treatment with $NaBH_4$ then reduces all the ketones, including those formed by the oxidation, to alcohols, and in particular it reduces the 21-deoxyketols to 17:20-glycols; these are then degraded to 17-ketosteroids by oxidation with sodium bismuthate. The determination is completed as described earlier (*Anal. Abstr.*, 1955, **2**, 2810). J. N. ASHLEY

2812. **Determination of urinary 17-hydroxycorticosteroids.** R. Devis and R. Vanek (*Ann. Endocrinol.*, 1954, **15**, 196–200).—*n*-Butanol generally contains chromogens which turn yellow when brought into contact with 12 *N* H_2SO_4. This reaction is also produced with the H_2SO_4 - phenylhydrazine reagent, but to a lesser degree. These disadvantages can be prevented by the addition of thiourea in an amount which does not interfere with the determination of cortisone and of Reichstein's substance S.

CHEM. ABSTR.

2813. **A method for the fractionation and measurement of 17-ketosteroids in human plasma.** C. J. Migeon and J. E. Plager (*J. Clin. Endocrinol.*, 1955, **15** [6], 702–714).—Dehydro*epi*androsterone (DHA) and androsterone are determined in 25 ml of plasma. The plasma is extracted with ethanol; after removal of solvent the residue is dissolved in water and the aq. soln. is continuously extracted with ether at pH 0·8 for 48 hr. The ether soln. is washed with $NaHCO_3$ and water and the ether is removed; the residue is chromatographed on Florisil columns and phenols are removed with NaOH. The DHA and androsterone are isolated by paper chromatography and determined by micro-Zimmermann reaction.

H. F. W. KIRKPATRICK

2814. **The Zimmermann reaction for the micro-determination of neutral 17-ketosteroids in urine.** E. J. Charollais (*Bull. Soc. Chim. Biol.*, 1955, **37** [2–3], 299–305).—The Zimmermann reaction depends on the fact that any compound containing a $-(CH_2{\cdot}CO)-$ group when treated with *m*-dinitrobenzene and KOH in an appropriate medium produces a more or less coloured substance whose concn. can be determined spectrophotometrically. *Procedure*—Samples of dried extracts of urine (> 40 μg,) containing < 5 μg of neutral 17-ketosteroids are treated with 0·2 ml of 2-methoxyethanol (**I**) and 0·2 ml of 2 per cent. *m*-dinitrobenzene in the same solvent and 0·2 ml of 3·0 *N* KOH in dry methanol. The colour develops in the dark at 45° ± 0·5° C in 45 min. After being cooled in ice, the mixture is diluted with 4 ml of **I** and transferred to the 10-mm cell of an S.P.600 Unicam spectrophotometer. The optical density is measured at 505 mμ, the results being expressed in μg of dehydro*iso*androsterone. By using specially purified reagents, reproducible results have been obtained in some 500 determinations on extracts of guinea-pig's urine, with an error not exceeding 10 per cent. P. HAAS

2815. **A comparison of urinary Zimmermann chromogens by Girard fractionation and by Allen's method of correction.** E. Chang and W. R. Slaunwhite, jun. (*J. Clin. Endocrinol.*, 1955, **15** [6], 767–770).—From a study of the absorption spectra of crude, ketonic and non-ketonic residues it is concluded that acceptance of the values for 17-ketosteroids obtained on ketonic residues as absolute is unwarranted. Values given by crude residues with Allen's method of correction (*Brit. Abstr. C*, 1950, 452) appear to give as true an approximation to the true excretion.

H. F. W. KIRKPATRICK

2816. **A method for the determination of urinary pregnanediol.** A. Klopper, E. A. Michie and J. B. Brown (*J. Endocrin.*, 1955, **12** [3], 209–219).—A new chromatographic procedure for determining small amounts of pregnane-3α:20α-diol in urine is described. The method involves hydrolysis with dil. HCl, extraction with toluene, a new oxidation step requiring 4 per cent. $KMnO_4$ in *N* NaOH, chromatography on alumina (grade 4), acetylation, a second chromatography on alumina and, finally, measurement at 430 mμ of the colour developed in 17 hr. at 25° C with conc. H_2SO_4. The method, which is considered highly selective for pregnanediol, gives a 94 per cent. mean recovery of known amounts of pregnanediol added to urine when the level is more than 0·5 mg per 24-hr. sample, with a difference range of 0 to 0·36 mg (mean 0·12 mg) of pregnanediol per 24 hr. between duplicate determinations. The sensitivity, accuracy and convenience of the method are considered and the significance of results obtained from male, proliferative-phase female and post-menopausal urine is discussed. W. H. C. SHAW

2817. **Determination of hydrocortisone.** C. R. Szalkowski, M. G. O'Brien and W. J. Mader (*Anal. Chem.*, 1955, **27** [6], 944–946).—A method for the identification and determination of hydrocortisone in substance, in mixtures with cortisone, and in pharmaceutical preparations is based on the yellow colour, with a maximum absorption at 470 mμ, produced by hydrocortisone in a mixture of sulphuric and glacial acetic acids. The effects of acetic acid concn., temp. and time are described. The method is not specific for hydrocortisone.

O. M. WHITTON

2818. **Determination of *p*-aminosalicylic acid in biological fluids.** M. V. Komendantova (*Bytull. Eksp. Biol. i Med.*, 1954, **38** [8], 74–79).—The method is based on a reaction between *p*-aminosalicylic acid (**I**) and sulphanilic acid, while sulphanilamide and *p*-aminobenzoic acid, which may be present in the fluid, remain unchanged. A 0·2-ml sample of blood is mixed with 1·4 ml of H_2O and deproteinised with 0·4 ml of trichloroacetic acid soln. (aq. 15 per cent.) (**II**). The mixture is filtered

or centrifuged and 1 ml of the filtrate is mixed with 0·6 ml of a freshly prepared diazo reagent (0·4 ml of 1 per cent. aq. sulphanilic acid soln., 0·1 ml of **II** and 2 drops of 5 per cent. $NaNO_2$ soln. are mixed and set aside for 10 min. before use) and 1·25 ml of saturated sodium acetate solution (aqueous). The colour is measured after 5 to 10 min. in a colorimeter and compared with standards. To determine **I** in the gastro-intestinal tract, the tissue is placed in 10 ml of 10 per cent. NaOH soln. and incubated at 50° C for 30 to 40 min. The hydrolysate is neutralised with 5 per cent. HCl and diluted to 50 ml. A 10-ml aliquot is deproteinised with 2 ml of **II** and 5 ml are used for the determination. The sensitivity is $<$ 1 mg per 100 ml. CHEM. ABSTR.

2819. **Colorimetric micro-determination of *iso*-nicotinoylhydrazine (isoniazid) in blood and other biological fluids.** M. Yantchitch (*Ann. Biol. Clin.*, 1954, **12**, 328–329).—A method depending on the reaction between the hydrazide function and vanillin in an acid medium yielding a yellow colour is described. *Procedure*—Precipitate proteins from serum with an equal vol. of aq. 20 per cent. trichloroacetic acid and filter. To 1 ml of the filtrate add 1 ml of vanillin in ethanol (2 per cent.) and measure the extinction at 420 mμ. A blank is run with the reagents, and standards of 1 to 25 μg per ml of the hydrazide are used. CHEM. ABSTR.

2820. **Chemical determination of isoniazid in pleural exudates.** W. Wareska (*Polski Tygod. Lekar.*, 1953, **8** [51], 1736; *Referativnyĭ Zh., Khim., Biologichekaya Khimiya*, 1955, Abstr. No. 2354).—A method for the determination of isoniazid in pleural exudates is based on its reaction with NH_4VO_3. A sample of the exudate is centrifuged for 10 min. at 3000 r.p.m. with an equal volume of trichloroacetic acid, and 1 ml of a soln. of NH_4VO_3 (0·25 g of NH_4VO_3, 20 ml of N H_2SO_4, and water to 100 ml) and 2 ml of water are added to 2 ml of the clear liquid. The extinction at 470 mμ is then measured. With isoniazid-free exudates, the extinction is insignificant. Exudates from patients treated with isoniazid contain 10 to 440 mg per 100 ml of isoniazid. E. HAYES

2821. **Continuous and simultaneous micro-determination of carbon dioxide and oxygen by a modified Warburg apparatus.** L. Chapon (*Brasserie*, 1955, **10** [102], 43–47).—The method is applicable wherever the maintenance of a concn. of CO_2 over the respiring tissue is unnecessary, and depends on the periodic micro manometric measurement at constant pressure of the O, and the determination of CO_2 by changes in electrical conductivity of $\simeq$ 0·05 N $Ba(OH)_2$. The modifications in the apparatus consist in the fitting of the leads for a pair of platinum electrodes through the vertical neck of the Warburg flask, the provision of a small centrally pivoted tubular vessel, which contains the aq. $Ba(OH)_2$ (0·6 ml) in which the electrodes are immersed, and a pivoting pin fused into the centre of the base of the flask. The continuous breaking of the film of $BaCO_3$ forming on the surface of the aq. $Ba(OH)_2$ is ensured by the attachment to the side of the tubular vessel of a weight, which causes adequate agitation of the contents while the flask is being regularly oscillated. Experimental confirmation of the accuracy of the method, directions for the calibration of the apparatus, and working details are given. P. S. ARUP

2822. **Continuous rapid infra-red carbon dioxide analysis [in respiratory studies].** C. R. Collier, J. E. Affeldt and A. F. Farr (*J. Lab. Clin. Med.*, 1955, **45** [4], 526–539).—Details are given for the adaptation of a direct-recording commercial infra-red CO_2 analyser, possessing a rapid response to changes in CO_2 concentration, to the study of respiratory CO_2 levels. Both inspired and expired air are sampled fractionally by means of a fine polythene nasal catheter, through which the sample is drawn into the analyser continuously by suction at a rate of 500 ml per minute. The instrument is calibrated with not less than three analysed mixtures of CO_2 and air differing by about 1 per cent. CO_2 concn. and covering the required CO_2 concn. range. The mean alveolar CO_2 tension, determined from the recordings, has a mean deviation of $-$0·9 mm of Hg (standard deviation $\pm$ 1·8 mm) when comparison is made with the CO_2 tension of arterial-blood samples taken at the same time. The limitations and use of the method for the proper control of artificial ventilation are discussed. W. H. C. SHAW

2823. **Quantitative determination of glucose and galactose.** H. Fisher, R. G. Hansen and H. W. Norton (*Anal. Chem.*, 1955, **27** [5], 857–859).—A rapid and sensitive method, based on the orcinol procedure of Brückner (*Hoppe-Seyl. Z.*, 1941, **268**, 163), is described for the simultaneous estimation of glucose and galactose in mixtures. To improve reproducibility, the reagents are mixed with the sample at ice-bath temp., heated for exactly 4 min. at 67° to 68° C while the colour develops, and re-cooled before measuring extinctions at 470 and 560 mμ. Results are usually within 30 μg for glucose and 10 μg for galactose in the sample range 0 to 150 μg of each sugar. A. R. ROGERS

2824. **Assay of thyrotrophin by the accumulation of radioactive iodine in the thyroid of the intact rat.** N. R. Stephenson, W. P. McKinley and P. J. Kavanagh (*Canad. J. Biochem. Physiol.*, 1955, **33** [3], 248–255).—Experiments described show that the thyroidal uptake of ^{131}I by intact weanling rats pretreated with iodinated casein serves as a satisfactory criterion of the response to exogenous thyrotrophin. The rats were fed on a diet containing 30 mg to 200 mg of iodinated casein per kg for 12 days. Each rat consumed $\simeq$ 5 g of the diet per day. The thyrotrophin preparation dissolved in 0·9 per cent. saline was injected subcutaneously at 9 a.m. and at 5 p.m. At least two dose-levels of the hormone were given, employing a log dose interval of 0·301. At 9 a.m. next day, each rat had an intraperitoneal injection of 0·5 ml of isotonic saline containing $\simeq$ 2 μC of carrier-free radioactive iodine (^{131}I). After 24 hr. without food or water the rats were chloroformed and the portion of the trachea with the entire thyroid gland attached was removed. The thyroid tissue was dissolved in 2 N NaOH solution containing 1 per cent. of KI and 0·1 per cent. of $NaHSO_3$; the vol. of the solution varied from 2 to 4 ml according to the dose of thyrotrophin. The number of counts per min. of a 1-ml aliquot of the digestion mixture was recorded and corrected for the background count and the "dead-time" of the Geiger - Müller counter used. A standard curve was plotted for each assay, relating the number of counts per min. per ml to various dilutions of the amount of ^{131}I administered to the rats. From these data, a factor was obtained for estimating the percentage of the injected dose of ^{131}I accumulated by each rat thyroid in 24 hr.

Graded doses of thyrotrophin provided a linear log dose - response line over the range 0·01 to 0·08 U.S.P. unit. The response approached a maximum value at dose levels above 0·16 U.S.P. unit. The thyroid gland of the female weanling rat retained, on the average, significantly more radioactive iodine than that of the male weanling rat when stimulated by thyrotrophin. Although the hormonal response was not correlated with the body weight of the rats within dosage groups, more precise assays were obtained by equalising the total weight of the rats in each dosage group before the assay. Relatively large doses of ^{131}I appeared to affect the precision of the assay adversely, but did not influence the response to thyrotrophin.

O. M. WHITTON

2825. **Preparation of extracts of urine and organs for estimation of free and conjugated noradrenaline and adrenaline.** U. S. von Euler and I. Orwén (*Acta Physiol. Scand.*, 1955, **33** [Suppl. 118], 1–9).—A method is described for the adsorption of catechol amines (adrenaline, noradrenaline) on Al_2O_3 at pH 8·5 and elution with H_2SO_4 (pH < 4). The extract is suitable for direct biological assay. The method has been applied successfully to urine and to extracts of organs prepared with trichloroacetic acid. The recovery of added catechol amines by biological assay is about 80 per cent. By subjecting the urine to acid hydrolysis for 20 min. at 100° C in *N* HCl before adsorption, the total yield was increased by up to 3 times in about 80 per cent. of the samples. The extracts obtained by elution with 0·5 *N* oxalic acid can be used for fluorimetric estimation of the catechol amines.

O. M. WHITTON

2826. **Fluorimetric estimation of noradrenaline and adrenaline in urine.** U. S. von Euler and I. Floding (*Acta Physiol. Scand.*, 1955, **33** [Suppl. 118], 45–55, 57–62).—A method for the fluorimetric estimation of adrenaline and noradrenaline in urine is described. The urine extracts are prepared by adsorption on Al_2O_3 at pH 8·5 and elution with 0·3 *N* oxalic acid. The catechol amines in the extracts are oxidised to adrenochrome and noradrenochrome at pH 3·5 and 6·0 with $K_3Fe(CN)_6$; the oxidation at pH 3·5 is enhanced by the addition of $ZnSO_4$. After molecular rearrangement of the oxidised product to the fluorescent compound by means of strong alkali and stabilisation with ascorbic acid, the fluorescence intensities are measured. At pH 6·0 both adrenaline and noradrenaline are completely oxidised and at pH 3·5 adrenaline plus about 4 per cent. of the noradrenaline. From these data and the relative fluorescence of adrenaline and noradrenaline the amounts of the two compounds can be calculated.

O. M. WHITTON

2827. **Determination of nucleic acids in animal tissues.** G. Ceriotti (*J. Biol. Chem.*, 1955, **214** [1], 59–70).—The colour reaction of deoxyribonucleic acid with indole (Ceriotti, *Brit. Abstr. C*, 1953, 215) is applied to the determination of this acid in animal tissues. The results agree well with those obtained by the diphenylamine reaction (Dische, *Brit. Abstr. A*, 1930, 632); the two methods are equally precise. The indole method is limited, but is useful when only very small amounts of tissue are available. An improved method for the determination of pentosenucleic acid is based on the determination of pentose with the orcinol reagent (Barrenscheen and Peham, *Brit. Abstr. A III*, 1942, 952). A comparison of methods for the determination of nucleic acid shows that determination of sugars and P gives only relative values, at least for pentosenucleic acid. These methods may be used alone for comparison of the same organ or tissue; otherwise a simultaneous determination by a u.v. spectrophotometric method is advisable. The u.v. method at present provides the best approach to the real values.

J. N. ASHLEY

2828. **Use of an ion-exchange resin for tissue hydrolysis in the determination of hexosamine.** P. A. Anastassiadis and R. H. Common (*J. Sci. Food Agric.*, 1955, **6** [4], 229–231).—Hydrolysis of tissue samples with Dowex-50 resin in 0·05 *N* HCl, followed by elution of the hexosamine with 2 *N* HCl and direct application of the Elson and Morgan procedure (*Biochem. J.*, 1933, **27**, 1824) to the eluate, gave results comparable to, but about 10 per cent. lower than, those obtained by tissue hydrolysis with 4 *N* HCl for 4 hr. and subsequent application of a modified Elson and Morgan procedure already described (*Canad. J. Chem.*, 1953, **31**, 1093), which included corrections for interference by sugars and by humin. In the former method the necessity of correcting for interference by interactions between sugars and amino acids and by humin is reduced or avoided. A procedure for various freeze-dried, avian tissues is described in detail, in which 15 to 30 mg of tissue heated with Dowex-50 resin (1 pt.) in 0·05 *N* HCl (4 pt.) for 24 hr. are used. The resin (on top of a glass-wool plug) is washed with distilled water and this liquid is discarded; 10 ml of 2 *N* HCl are then passed through the resin column to elute the hexosamine, which is collected in a 10-ml calibrated flask. After suitable treatment, portions of the eluate are read at 530 mμ.

S.C.I. ABSTR.

2829. **Qualitative determination of amino acids in protein hydrolysates by circular-paper chromatography.** I. Oreskes and A. Saifer (*Anal. Chem.*, 1955, **27** [5], 854–856).—A circular-paper chromatographic technique is described which permits identification within 24 hr. of all 19 amino acids usually found in protein hydrolysates, except for the two leucines, which are determined as a pair. Two separate chromatograms are run for each hydrolysate, with phenol - *iso*propanol - water (70:5:25, by wt.) in the presence of NH_3 vapour, and butanol - acetic acid - water (40:10:50, by vol.), as the respective developing solvents. After being washed with acetone to remove phenol, and drying, each chromatogram is cut into halves. One half is dipped into ninhydrin and the other in isatin as the two colour reagents. The reproducibility of R_F values compares favourably with the best previously reported with buffered filter-papers. Quant. applications are under investigation.

A. R. ROGERS

2830. **Separation of dinitrophenols from dinitrophenylamino acids and peptides.** F. Turba and G. Gundlach (*Biochem. Z.*, 1955, **326** [5], 322–324).—The following method permits accurate recovery of dinitrophenyl derivatives of amino acids. The amino acid (1 μmole) dissolved in water (0·2 ml) is mixed with saturated $NaHCO_3$ soln. (0·5 ml) and methanol (1 ml) containing fluoro-2:4-dinitrobenzene (0·01 ml). After being shaken for 2 hr., the mixture is shaken twice with ether (2 ml), acidified with 6 *N* HCl and extracted with ethyl acetate (3 × 1·5 ml). After evaporation of the ethyl acetate in an air-stream at 40° C, the residue is dissolved in 0·5 ml of methanol and transferred to an anionotropic column of Al_2O_3 with the aid of a further 0·5 ml of methanol. The

phenol is quantitatively removed by 2 per cent. acetic acid, leaving the derivatives of the amino acid, which can be eluted with 0·1 *N* NaOH soln. On making up to a known volume with 1 per cent. $NaHCO_3$ soln., the extinction can be determined at 350 mμ. G. W. CAMBRIDGE

2831. **The use of borate buffer in paper electrophoresis of serum.** R. Consden and M. N. Powell (*J. Clin. Pathol.*, 1955, **8** [2], 150–152).—Borate buffer gives a well-marked separation of the β-globulins; thus fresh serum shows two and occasionally three bands in this zone. It has the disadvantage of increasing the mobility of the α_1-globulin to that of albumin. A mixed barbitone-borate buffer consisting of equal vol. of the 0·05 *M* barbitone buffer of Durrum (*J. Amer. Chem. Soc.*, 1950, **72**, 2943) and a buffer prepared by mixing 3·5 vol. of 0·1 *M* boric acid with 1 vol. of 0·1 *M* NaOH is recommended for routine use, since it combines the advantages of both types of buffer. H. F. W. KIRKPATRICK

2832. **The reliability of the determination of urinary proteins by electrophoresis on filter-paper.** D. Wolvius and J. C. M. Verschure (*J. Clin. Pathol.*, 1955, **8** [2], 140–143).—For paper electrophoresis of urine, 20 to 40 ml are concentrated to 2 to 0·2 ml in small Cellophane bags of about 40-ml capacity at 4° C by dialysis against 15 per cent. aq. carboxymethylcellulose, or alternatively, 25 per cent. aq. poly(vinylpyrrolidone). The error of the determination of the albumin fraction due to the paper blank and trailing increases with diminishing amounts of protein, and at least 0·6 mg of protein should be present in the sample used for the electrophoresis. H. F. W. KIRKPATRICK

2833. **The developing process in the paper chromatography of proteins.** K. Macek (*Chem. Listy*, 1954, **48** [8], 1181–1188).—An investigation is presented of the chief factors influencing the chromatographic behaviour of enzymes on paper, especially the concentration gradient of the solvent system, the concentration gradient of NaCl and the saturation of the chamber atmosphere. Conclusions on the probable mechanism of the separation of proteins by paper partition chromatography are drawn. G. GLASER

2834. **A simple technique for counting milligram samples of protein labelled with ^{14}C or ^{35}S.** J. Garrow and E. A. Piper (*Biochem. J.*, 1955, **60** [3], 527–528).—A combination of a gas-flow counter, a thin sample film technique, and a compact scaler-E.H.T.-timer unit is described for determination of very small amounts of ^{35}S activity. The apparatus is simple to operate and maintain and will measure activity of the order of 10^{-11} curies in a small sample of tissue. The counting gas is He and the counter is made of nickel-plated brass. A biopsy sample is homogenised in saline and the protein is pptd. with 5 per cent. w/v trichloroacetic acid. The defatted, dried sample is dissolved in *N* NaOH, and 20 to 30 cu. mm of the solution are transferred by pipette on to a circle of lens paper (3 sq. cm) placed on a rhodium-plated planchette. After drying immediately, it is inserted into the counter and the activity is determined. The results are reproducible within ± 5 per cent. J. N. ASHLEY

2835. **A nephelometric method for the estimation of cholesterol.** E. G. Stenger (*Klin. Wochschr.*, 1955, **33** [21–22], 534–536).—Centrifuge tubes marked at 6 ml are used. To prepare a standard curve, transfer aliquots of a standard soln. of cholesterol in acetone-abs. ethanol (1:1), containing up to 1·6 mg of cholesterol, by pipette, into centrifuge tubes, and make up to 6 ml with solvent. Add 2 ml of dist. water and 1 ml of digitonin soln. (0·6 per cent. in the acetone-ethanol mixture), and set aside for 1 hr. Centrifuge and take off the clear supernatant liquid down to the 6-ml mark; disperse the ppt. by stirring with a small glass rod and read the turbidity in a 0·5-cm cell, a blue or yellow filter being used. To determine total cholesterol in serum, add 0·5 ml dropwise with gentle shaking to 5 ml of acetone-ethanol, filter and wash with 3 ml of solvent. To the filtrate add 0·5 ml of sodium methoxide soln. (1 g of bright sodium metal dissolved in 25 ml of methanol cooled in ice; methanol lost by evaporation is replaced and the soln. is kept in the ice-chest); set aside at room temp. for 1 hr. to hydrolyse cholesteryl esters, then add 2 drops of phenolphthalein soln. (1 per cent. in 96 per cent. ethanol) and neutralise with dil. HCl. Add a few drops of glacial acetic acid, 2 ml of water and 1 ml of digitonin soln., and proceed as for the standards. H. F. W. KIRKPATRICK

2836. **Optical analytical studies on steroids. Reducing characteristics of hydroxylated and ketonic steroids toward blue tetrazolium.** A. S. Meyer and M. C. Lindberg (*Anal. Chem.*, 1955, **27** [5], 813–817).—This is a study of the reducing properties towards 3:3′-(3:3′-dimethoxy-4:4′-diphenylene)di-(2:5-diphenyltetrazolium chloride) (blue tetrazolium) reagent of a number of Δ^4-3-ketosteroids with hydroxyl or keto groups present in various positions in the molecule. Depending on their location and configuration, these groups give rise to varied rates and intensities of colour formation. Owing to the complexity of the reaction, the diagnostic value of the rate measurements for structural characterisation of micro-quantities of steroids is limited. A. R. ROGERS

2837. **Rapid estimation of amylase activity of serum by turbidimetry.** O. Peralta and J. G. Reinhold (*Clin. Chem.*, 1955, **1** [3], 157–164).—The method described is adapted from that of Waldron (*Brit. Abstr. C*, 1952, 19) for amylase in pancreatic juice. The amylase activity of serum is estimated by measuring the decrease in absorption at 660 mμ of 5 ml of buffered starch suspension after incubation at 38° C for 5 min. with 1 ml of serum. H. F. W. KIRKPATRICK

2838. **A spectrophotometric determination of trypsin and chymotrypsin.** G. W. Schwert and Y. Takenaka (*Biochim. Biophys. Acta*, 1955, **16** [4], 570–575).—By the use of tyrosine esters and benzoylarginine esters as substrates for chymotrypsin and trypsin, respectively, differential spectrophotometry (Hakala and Schwert, *Biochim. Biophys. Acta*, 1954, **16**, 489) has been employed for the estimation of these enzymes. *Chymotrypsin*—A 0·001 *M* soln. of L-tyrosine in 0·05 *M* phosphate buffer (pH 6·5) (3 ml) and a chymotrypsin soln. in 0·001 *M* HCl (0·2 ml) are placed in the control cuvette of a Beckman DU spectrophotometer at 25° C, adjusted to give an optical density of zero with this cuvette in the light path. In the test cuvette is placed 0·001 *M* L-tyrosine ethyl ester hydrochloride in the same buffer as above (3 ml) and at zero time chymotrypsin (0·2 ml) is added. The optical density is determined at 282 mμ at 15-sec. intervals until control and test cuvettes give the

same optical density at the completion of the reaction; 1·5 to 15 μg of chymotrypsin may be estimated by this method. *Trypsin*—The spectrophotometer is adjusted to give an optical density reading of zero at 280 mμ with a 0·001 *M* soln. of N-benzoyl-L-arginine ethyl ester in 0·05 *M* tri-(hydroxymethyl)methylamine in the light path. Addition of trypsin as a 0·001 *M* soln. in HCl (0·2 ml) causes an initial decrease in optical density owing to dilution, followed by a gradual increase, linear with time, until it is the same as that of the test cuvette, which contains 0·001 *M* N-benzoyl-L-arginine in the buffer given above (3 ml) and trypsin solution (0·2 ml). By this method 1·5 to 20 μg of trypsin can be estimated. G. W. CAMBRIDGE

2839. **Potentiometric technique for determining the activity of pancreatic lipase.** P. Desnuelle, M. J. Constantin and J. Baldy (*Bull. Soc. Chim. Biol.*, 1955, **37** [2–3], 285–290).—The activity of the enzyme is determined on a substrate consisting of an emulsion of olive oil stabilised by gum acacia and activated by sodium tauroglycocholate and $CaCl_2$, and buffered with tri(hydroxymethyl)methylamine. The mixture is placed in a thermostat at 37° ± 0·5° C, and a glass electrode and the electrode of a direct-reading pH meter are inserted. The soln. is gently agitated by a mechanical stirrer and a slow stream of CO_2-free nitrogen is blown over the surface of the liquid, the pH being adjusted to 8·2 by addition of carbonate-free NaOH soln. The enzyme soln. is then added. When the needle of the pH meter passes the graduation 8·0, sufficient 0·1 *N* NaOH is added to bring it back to 8·2 and the exact time is noted for the needle to return to the 8·0 mark. Several readings of this kind yield a curve of equiv. of acid liberated by the lipase, as a function of the time. The expt. results lie on perfectly straight lines and are reproducible and strictly proportional to the amount of enzyme used.
P. HAAS

2840. **The effect of salts on the estimation of cholinesterase activity.** B. N. Smallman and L. S. Wolfe (*Enzymologia*, 1954, **17** [3], 133–144).—The activation of cholinesterase (**I**) by added salts differs when estimated by the manometric and titrimetric methods, owing to the presence of $NaHCO_3$ in the manometric method. In comparison with most of the other sodium salts studied, $NaHCO_3$ has a depressant effect on activity of **I**; phosphate buffer has a similar effect. The activation of **I** by added salts also varies with the concn. of tissue homogenate (probably because of the presence of endogenous salts) and of acetylcholine.
A. R. ROGERS

2841. **A field test for the assay of human whole-blood cholinesterase.** D. R. Davies and J. D. Nicholls (*Brit. Med. J.*, 1955, 1373–1375).—Blood (0·02 ml) collected in a haemoglobin pipette is washed into 1 ml of bromothymol blue soln. pH 7·7. Acetylcholine soln. (0·5 ml) is added and the exact time-interval between the addition and the change of colour of the mixture to deep orange is noted as a measure of the cholinesterase activity. The reaction time varies markedly with temp., and to overcome this difficulty in field tests a chart has been constructed relating the results of the test at temp. between 10° and 30° C with the degree of poisoning by anticholinesterases.
H. F. W. KIRKPATRICK

See also Abstracts 2614, 2751, 2762, 2845, 2910, 2912.

Drugs

2842. **Selective detection of ephedrine and adrenaline by drop reactions.** F. Feigl and H. E. Feigl (*Helv. Chim. Acta*, 1955, **38** [2], 459–462).—Both ephedrine and adrenaline or their salts, when warmed with 2 *N* NaOH, evolve methylamine, which forms a yellow condensation compound, insol. in water, with 1-chloro-2:4-dinitrobenzene (**I**). By using the special micro-apparatus for "hanging drops" (Feigl, "Spot Tests," Vol. II, Elsevier, 1954, p. 40) a small quantity of the sample to be tested is introduced into the capsule and treated with 1 drop of 2 *N* NaOH, a hanging drop of a saturated alcoholic soln. of **I** being suspended above. The closed apparatus is then heated in a water bath for 10 min. The yellow condensation compound, if present only in very small amount, may be washed with chloroform and shaken with dil. acetic acid. A yellow colour remaining in the chloroform layer is characteristic. Limits of detection in a drop (0·05 ml) are 7 μg for ephedrine and 8 μg for adrenaline. Ephedrine, if in admixture with adrenaline, can be detected by this method provided that it is previously extracted from the mixture with ether, in which adrenaline is insol. The limit of detection is 5 μg of ephedrine. A delicate and selective test for adrenaline consists in adding a saturated alcoholic soln. of *o*-dinitrobenzene to an acid soln., making alkaline and warming for a short time, when a violet colour is formed, owing to the reducing action of adrenaline on *o*-dinitrobenzene.
P. HAAS

2843. **Photometric determination of adrenaline and other catechol derivatives in finished pharmaceutical products.** J. Richter (*Z. anal. Chem.*, 1955, **145** [5], 334–336).—The solution containing adrenaline is made up to 10 ml with $NaHSO_3$ (0·2 per cent.), and Fe citrate solution (0·1 ml) and buffer solution (1 ml) are added. The extinction is measured in a 2-cm cell after 30 min. A calibration curve is given. In the presence of Falicain (β-piperidinoethyl *p*-propoxyphenyl ketone), at the end of 30 min. add 11 ml of ethanol and double the E value obtained. The calibration curve can be employed for other catechol derivatives by using the following factors: Corbasil (3:4-dihydroxynorephedrine) (1); noradrenaline (0·906); isoprenaline (1·41). Results of determinations on pharmaceutical products are given.
R. STERN

2844. **Polarography of papaverine.** V. D. Bezuglyi (*Zh. Obshch. Khim.*, 1954, **24** [12], 2190–2195).—Polarographic reduction of papaverine in 0·02 *M* tetramethylammonium hydroxide in 10 per cent. ethanol, at $E_{\frac{1}{2}}$ of 1·92 to 1·95 V, involves transfer of 4 electrons; the diffusion coeff. $D = 0{\cdot}785 \times 10^{-3}$ sq. cm per sec. Papaverine and codeine present together are determined by polarography successively in 10 and 70 per cent. ethanol; in the latter solvent the codeine wave is suppressed.
R. TRUSCOE

2845. ***iso*Nicotinic acid hydrazide [isoniazid] as a reagent for determination of Δ4-3-ketosteroids. Determination of progesterone and testosterone propionate in oil solutions.** E. J. Umberger (*Anal. Chem.*, 1955, **27** [5], 768–773).—A new colour reaction for the quant. determination of Δ4-3-ketosteroids is described, based on the formation of a yellow colour with isoniazid in absolute ethanol acidified with HCl. The method has been applied

to soln. of testosterone propionate (**I**) and progesterone (**II**) in vegetable oil, and compares favourably with the U.S.P. biological method and the semicarbazide method of Madigan, Zenno and Gordon (*Anal. Chem.*, 1948, **20**, 174). *Reagent*—A mixture of isoniazid (0·5 g) and conc. HCl (0·625 ml) in absolute ethanol (1 litre) is used. *Procedure*—Evaporate a soln. of the oil (containing $\simeq$ 50 μg of the steroid) in ethanol, shake the residue with the reagent (4 ml), and measure the extinction at 380 mμ in 1-cm cells against a reagent blank after 1 hr. at room temp. Compare with a similarly treated standard soln. of the steroid in ethanol. The molar extinction coeff. is $\simeq$ 11,000. If the oil contains $>$ 10 mg of steroid per ml, and a sample of the same oil is not available as an internal blank, chromatographic separation is necessary. Prepare a soln. of the oil (containing 0·5 mg of steroid) in a 2:1 mixture of *iso*octane and $CHCl_3$, add to a column of 60 to 100-mesh Florisil (4·25 g), and develop with the same solvent mixture (100 ml). Elute **I** with *iso*octane - $CHCl_3$ (1:1) (200 ml), and then **II** with $CHCl_3$ (150 ml). Evaporate aliquots of the two eluates separately and complete the determinations as described above. Details are also given of a method for the identification of **I** in oil, and of the preparation and m.p. of the *iso*nicotinoylhydrazones of eight ketosteroids. A. R. Rogers

2846. **Paper chromatography of chlortetracycline [aureomycin].** M. Dohnal and J. Bialá (*Chem. Listy*, 1954, **48** [8], 1261–1262).—Descending chromatography on Whatman paper No. 1 or 4 is a convenient and rapid method for the qual. and quant. determination of chlortetracycline in 1 to 3-μg samples from the various stages of its manufacture, including a direct determination of the antibiotic in the fermentation liquors. In the recommended solvent system, *n*-butanol (4 parts), acetic acid (1 part) and water (5 parts), the R_F value of chlortetracycline is 0·56. The zones are detected by their yellow fluorescence in u.v. light, or, quantitatively, by bio-autography. G. Glaser

2847. **Determination of erythromycin by ultraviolet spectrophotometry.** J. B. Tepe and C. V. St. John (*Anal. Chem.*, 1955, **27** [5], 744–746).—Colour reactions previously described for the analysis of erythromycin (**I**) are not applicable to process samples, because of lack of sensitivity and specificity. After dilute alkaline hydrolysis, **I** shows strong absorption at 236 mμ with an $E^{1\%}_{1\,cm}$ of 85. This has been made the basis of a spectrophotometric assay; a blank inactivated with dil. acid is used to correct for the u.v. absorption of impurities. The results agree with those by microbiological turbidimetric assay, and the precision and sensitivity are good. *Procedure*—Prepare an aq. soln. of the sample so that a 5-ml aliquot contains $\simeq$ 500 μg of activity. Non-aqueous soln. should be evaporated to dryness and the residue dissolved in methanol and diluted with water; alternatively, extract the **I** from water-immiscible solvents with a 1 per cent. aq. soln. of diglycollic acid, and dilute the aq. phase. Heat the soln. (5 ml) with 0·05 *N* NaOH (1 ml) at 100° C for 5 min., cool, dilute to 10 ml and measure the extinction at 236 mμ within 20 min. For the blank, the sample soln. (5 ml) is treated with 0·05 *N* H_2SO_4 (0·5 ml) at room temp. for 1 hr., then heated with 0·05 *N* NaOH (1·5 ml) at 100° C for 5 min.; the procedure is then as described above. A. R. Rogers

2848. **Statistical evaluation of the paper-disc-plate method for neomycin assay.** E. R. Garrett and G. M. Savage (*Antibiot. & Chemother.*, 1955, **5** [5], 273–280).—From a statistical study of the method it is concluded that at a level of 20 μg per ml and measuring four zones, each on a different agar plate, the standard error with *Bacillus subtilis* as test organism is 13 per cent. compared with 29 per cent. with *Klebsiella pneumoniae*. No significant variations were found among operators or among dilutions by the same operators provided that the buffer-salt concentration was maintained at the critical level, any deviations from which affected reproducibility. It is found generally more economical to increase the number of days on which a sample is assayed than to increase the number of zones measured on a given day, and expressions relating standard error and cost per assay are given. W. H. C. Shaw

2849. **Polarography of barbituric acid derivatives. IV. Suppression of maxima by derivatives of thiobarbituric acid.** P. Zuman (*Chem. Listy*, 1954, **48** [7], 1020–1024).—Owing to their adsorption on the dropping-mercury electrode, 5-alkyl derivatives of thiobarbituric acid suppress oxygen maxima and the anodic maxima of ascorbic acid. The relation between the suppressing power and the adsorbability of their salts with mercury was studied, and an approx. linear relationship was found between the suppressing ability of these compounds and their molecular weight. G. Glaser

2850. **Application of ion-exchange resins in medicinal analysis. I, II. Determination of calcium gluconate.** H. Watanabe (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [1], 1–6).—To test Ca gluconate (for injections), the soln. ($\simeq$ 0·1 *M*) is passed through a column of the ion-exchange resin Amberlite IR-120 (H) and the eluate is titrated with 0·1 *N* NaOH soln. (phenolphthalein). Experimental conditions, including the rate of flow (1·0 to 8·5 ml per sq. cm per min.) and the amount of washing water, were examined. The average deviation from the mean is $\simeq$ 1·0 per cent. The time occupied by an estimation is $<$ 50 min. Other ingredients (*e.g.*, stabilisers such as citric acid, boric acid, borax and NH_4Cl) vitiate the determination. K. Saito

See also Abstracts 2615, 2746, 2770, 2861.

Food

2851. **Determination of pectin in sugar products.** M. Vender (*Listy Cukrovarn.*, 1953, **1**, 11–15; *Referativnýĭ Zh., Khim.*, 1955, Abstr. No. 714).—Pectin is determined by measuring the CO_2 formed when it is heated with acids (Dickson *et al.*, *J. Amer. Chem. Soc.*, 1930, **52**, 775). A weighed sample of material containing $\simeq$ 0·1 g of pectin is dissolved in 50 ml of HCl (12 per cent.) and the soln. is heated in a bath at 130° to 150° C; the CO_2 is absorbed in $Ba(OH)_2$ soln. and the conductivity is continuously recorded. Any carbon dioxide present in the HCl soln. is previously removed by heating the soln. to between 40° and 50° C under reduced pressure. If organic acids are present, they can be removed by washing the pectin with 60 per cent. ethanol containing 1 per cent. of HCl, followed by pure ethanol. For low contents of pectin, the sample is dissolved in water and twice its vol. of ethanol is added to the soln.; the determination is then carried out on the ppt. The rate of decomposition of pectin in solutions containing various amounts of HCl, KCl and NaCl

is studied at different temperatures; with 18 per cent. HCl extensive decomposition occurs.
E. HAYES

2852. **A study of the reproducibility of viscosity determinations using gelatin sols.** L. C. Lappas and E. P. King (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [3], 164–169).—A collaborative study (7 laboratories) of the testing procedure for the viscosity of gelatins initially and after heating for 17 hr. at 60° C is reported. Bone, calfskin and porkskin gelatin sols behave as Newtonian liquids for limited periods of time in the capillary-pipette test used. The coefficient of variation within analysts was 1·94 per cent. The variation between analysts averaged 2 to 3½ times the variation within analyses. There was evidence of consistent differences between laboratories; differences up to 9 per cent. in average determinations between individual laboratories were found. The largest differences were attributed to variations in the method of pipette calibration and in temp. control during the 17-hr. heating.
A. R. ROGERS

2853. **Estimation of insect fragments in maize.** W. D. Raymond, R. G. W. Spickett and J. B. Ward (*Colon. Pl. Anim. Prod.*, 1954, **4** [4], 334–335).—The A.O.A.C. method ("Methods of Analysis," 7th Ed., 1950, p. 716) for the estimation of insect fragments and extraneous matter is unsatisfactory for heavily infested samples of maize. Ten-fold differences in results are reported in a collaborative investigation on carefully sampled material. With decreasing wt. of sample, insect-fragment count increases. Insect-particle size may be partly responsible for differences in results. The A.O.A.C. method is modified by effecting a preliminary dilution with pure potato starch and hydrolysis with dil. acid before the flotation process. Certain other precautions are also noted.
S. C. JOLLY

2854. **Identification of α-lactalbumin in the electrophoretic pattern of milk-serum proteins.** B. L. Larson and R. Jenness (*J. Dairy Sci.*, 1955, **38** [3], 313–315).—Details are given of the electrophoretic analysis of milk-serum proteins and of the mobilities obtained for the various known and unknown component proteins. The behaviour of recrystallised α-lactalbumin during electrophoresis is studied, and the methods adopted for identifying the corresponding peak in the electrophoretic pattern of serum proteins are discussed.
W. H. C. SHAW

2855. **Reichert - Meissl value: its importance and limitations in the detection of foreign fats in butterfat.** G. K. Murthy (*J. Dairy Sci.*, 1955 **38** [3], 317–318).—The influence of breed, stage of lactation, feed, age, season, degree of nourishment and disease on the Reichert - Meissl value of butterfat is discussed. The effects of adulteration with other animal and vegetable fats are also considered, and it is concluded that other factors and analytical constants that have a relationship with the Reichert - Meissl value must be considered in fixing standards for a given dairy product.
W. H. C. SHAW

2856. **The application of thermodynamic methods of analysis to the detection of adulterated cocoa butter.** S. V. Vaeck (*Int. Choc. Rev.*, 1955, **10**, 20–21).—The methods used are that of Pichard, in which the fat (about 30 g) is contained in a vacuum flask and a cooling curve is plotted, and that of "crystallisation delay." In the latter method, 1 g of melted fat in a capillary tube is placed in a constant-temp. bath and the time noted for cloudiness to appear. Characteristic time - temp. curves are obtained for different fats. Both methods detect about 20 per cent. of adulteration in most cases, but fail to detect this amount of illipé butter.
B.F.M.I.R.A. ABSTR.

2857. **Separation of mineral oil - vegetable oil mixtures using adsorption columns.** R. P. Harker (*Chem. & Ind.*, 1955, [21], 592).—Two methods were found to be successful in separating the constituents of mixtures and emulsions of paraffin and olive oils. (*i*) Emulsions of the two oils, stabilised with non-ionic "Lissapol N," were passed through ion-exchange resin columns (in some cases, with powdered activated charcoal added) and then eluted with acetone - chloroform mixtures. Almost complete separation was achieved, the detergent remaining in the column. (*ii*) A solution of the mixed oils in light petroleum (boiling range 40° to 60° C) was applied to a column of chromatographic-grade alumina and eluted with solvent. Rapid and complete separation, with recovery > 97 per cent., was obtained. Assessment of the degree of separation was made by measurement of refractive index and i.r. absorption spectra. The techniques used were those described by Harker *et al.* (*Anal. Abstr.*, 1954, **1**, 1575) and Green *et al.* (*Anal. Abstr.*, 1955, **2**, 120).
S.C.I. ABSTR.

2858. **Quantitative determination of calcium pantothenate, calcium gluconate, riboflavine, sorbitol and choline preparations.** H. Wojahn and L. Kraft (*Dtsch. ApothZtg*, 1955, **95** [19], 443–444).—Methods are given for the quantitative determination of the following preparations. (*a*) *Ca pantothenate*—A 0·7-g sample is dissolved in 20 ml of H_2O and 25 ml of 0·1 *M* EDTA (disodium salt) (**I**) and 10 ml of an aq. NH_3 - NH_4Cl buffer soln. are added, giving a pH of 8 to 10. The excess of **I** is titrated with 0·1 *M* $ZnSO_4$ soln., with Eriochrome black T as indicator. Results are 98·65 to 98·91 per cent. of theoretical. Calcium gluconate may be similarly estimated, giving 8·92 to 8·94 per cent. of Ca (theoretical 8·94 per cent.). (*b*) *Ca gluconate*—To 45 mg dissolved by warming in 5 to 10 ml of H_2O are added 30 ml of 0·1 *N* $NaIO_4$ soln. The product is set aside for 3 hr., then 35 ml of 0·1 *N* Na_3AsO_3 and 2 ml of KI soln. (20 per cent.) are added, the final soln. being titrated against 0·1 *N* I soln., after 15 min. The accuracy of this method is 98·8 to 99·75 per cent. for Ca gluconate. Riboflavine, 99·36 to 101·36 per cent. of theoretical, and sorbitol, 99·46 to 100·0 per cent., are similarly estimated. (*c*) *Choline chloride*—To 45 mg dissolved in 10 ml of H_2O are added 8 to 10 ml of ammonium reineckate soln. (25 per cent.) and the product is set aside for 30 min., with cooling. The ppt. is filtered off and washed, then dissolved in 15 to 20 ml of acetone, diluted with 40 ml of H_2O and 1 ml of Fehling's soln. No. 2, and after 10 min. the soln. is gently boiled. The cooled soln. is treated with 20 ml of HNO_3, 15 ml of 0·1 *N* $AgNO_3$ soln., and ferric ammonium sulphate soln., then titrated with 0·1 *N* ammonium thiocyanate soln. The method gives results 99·6 to 100·2 per cent. of theoretical.
G. R. WHALLEY

2859. **The quantitative determination of ascorbic acid by paper chromatography.** R. Strohecker, W. Heimann and F. Matt (*Z. anal. Chem.*, 1955, **145** [6], 401–417).—Ascorbic acid may be quant. separated from cysteine, glutathione, reductone,

reductic acid, Fe^{++}, Zn^{++}, SO_3^{--} and $S_2O_3^{--}$, but not from *iso*ascorbic acid, by paper chromatography. The sample ($\simeq$ 20 μl containing $\simeq$ 2 μg of ascorbic acid) is applied to a 30-cm strip of filter-paper 2043b M (Schleicher and Schüll), and developed for 5 to 5½ hr. with the organic phase of a 4:6 mixture of butanol and water containing 2 per cent. of oxalic acid and a trace of KCN. R_F values are given for the substances mentioned. The use of acetic acid instead of oxalic acid, as previously suggested (*Anal. Abstr.*, 1954, **1**, 369) for qual. separation, causes losses. The ascorbic acid may be determined by elution with aq. oxalic acid (0·5 to 1 per cent.) in a stream of CO_2, and titration with 0·001 *N* 2:6-dichlorophenolindophenol. By reducing any dehydroascorbic acid with H_2S before chromatography, the total vitamin-C content may be determined in a similar manner. Undue delay must be avoided at all stages of the determination to avoid decomposition of the ascorbic acid (R_F value 0·23 to 0·26) to an unknown product with R_F = 0·08. A. R. ROGERS

2860. **Paper-chromatographic estimation of ascorbic acid and dehydroascorbic acid.** H. Schmidt and H. Staudinger (*Biochem. Z.*, 1955, **326** [5], 343–349).—Chromatograms are run with butanol-acetic acid-H_2O (4:1:5) in the presence of CO_2 for 5 hr. For qual. evaluation, the spots are revealed by contact photography under u.v. light, and further identification is achieved by treatment with 0·1 *N* oxalic acid, elution with water and examination of the absorption spectrum. For quant. evaluation, 20 to 60 μg of ascorbic acid should be used. The spots are identified as above, cut out, and transferred to a vessel containing 0·1 *N* oxalic acid (1 ml). After 20 min. the soln. is diluted with H_2O (5 ml) and after a further 10 min. the extinction is measured at 245 mμ. Estimation of dehydroascorbic acid is based on the same principles, but the pH of the solution must be between 2 and 3. Dehydroascorbic acid can be reduced with H_2S to ascorbic acid and estimated as such. G. W. CAMBRIDGE

2861. **Investigations into the *Euglena gracilis* method for quantitative assay of vitamin B_{12}.** H. P. Østergaard Kristensen (*Acta Physiol. Scand.*, 1955, **33** [2–3], 232–237).—Ross's modification of Hutner's method for the quant. determination of vitamin B_{12} with *Euglena gracilis* var. *bacillaris* was used in experiments which showed that the supernatant liquid from a centrifuged vigorously growing *Euglena* culture contains a thermolabile factor, which has a growth-inhibiting effect on *Euglena* cells when they are transferred to a freshly prepared medium containing vitamin B_{12}. Density and uniformity of growth are increased by washing and diluting the *Euglena* culture used for inoculation. The sensitivity and the accuracy of the method are thereby increased. O. M. WHITTON

See also Abstracts 2751, 2875.

Sanitation

2862. **Trapping of aerosols in taking samples of air from production sites.** D. N. Vaskevich and S. S. Gurvits (*Zavod. Lab.*, 1955, **21** [1], 33–34).—Experiments were carried out on aerosols produced by heating 1- or 2-naphthol in a porcelain dish. Filters of various pore-sizes were placed at different distances from the fog generator and the rate of suction of air through the filters was varied. The samples were removed from the filters by means of ethanol under suction. Particle sizes of material collected on a microscope slide were also determined. It is shown that there is a limiting rate of flow of air above which a filter becomes ineffective. Results for various filters, flow rates, etc., are tabulated. G. S. SMITH

2863. **Determination of hydrogen sulphide and sulphur dioxide in air. I. Errors in the iodimetric determination and their elimination.** Y. Kitano and H. Takakuwa (*Japan Analyst*, 1954, **3** [1], 7–10).—When air containing H_2S and SO_2 (each $\simeq$ 10 p.p.m.) is bubbled through 0·01 *N* iodine soln., a significant amount of iodine escapes. This iodine may be trapped almost quant. in a second bubbler containing a known amount of 0·01 *N* $Na_2S_2O_3$, which is connected to the first with a glass joint. The use of rubber tubing should be avoided. The distilled water and starch soln. used must be treated with 0·01 *N* iodine soln. until a very faint colour remains. It is also advantageous to keep the first bubbler ice-cooled during the passage of air. K. SAITO

2864. **Determination of total mineral matter in water analysis.** K.-E. Quentin (*Z. anal. Chem.*, 1955, **146** [1], 18–29).—Waters containing less than 1 g per kg of mineral matter gave fairly good correlation between total mineral matter, as obtained by complete analysis, and determination of non-volatile residue at 105° C, when corrected for the content of bicarbonate which is determined by titration with 0·1 *N* HCl, with a suitable indicator. For higher mineral content, cationic exchangers are recommended. Either the total acids less CO_2 are titrated and the bicarbonate calculated, or the bicarbonate is first neutralised by HCl before the water is passed through the cationic exchanger, and the total acids in the filtrate are titrated with 0·1 *N* NaOH. The mineral matter is then calculated as milli-equivalents. Fairly good correlation with mineral matter by complete analysis was obtained. The use of "sulphate control" (conversion of the residue into sulphates) and anionic exchangers are discussed but not recommended. R. STERN

2865. **Determination of dissolved oxygen.** D. Parkhouse (*Chem. & Ind.*, 1955, [21], 588–589).—Where the determination of dissolved O in water involves a correction for reducing substances present, results can be checked by passing the sample through a "mixed bed" ion-exchange resin to remove ionisable reducing substances, followed by determination of dissolved O in the eluate. S.C.I. ABSTR.

2866. **An indirect colorimetric determination of sodium in natural water.** T. Kato, Y. Okiyama and T. Nomura (*Japan Analyst*, 1955, **4** [2], 106–107).—The sample (250 to 500 ml) is evaporated to dryness, the residue is extracted with a small amount of water and made up to 10 ml. A 1-ml portion is treated with magnesium uranyl acetate (one mole per litre of *N* acetic acid) (1 ml) and 95 per cent. ethanol (2 ml). The ppt. is dissolved in water, made basic with NaOH (30 per cent.) (7 ml) and made up to 25 ml with titanium yellow reagent (0·1 per cent.) (0·2 ml). The pink colour is compared with that of the standard after 10 min. Potassium salts ($>$ 3 mg of K per ml of the soln. that is treated with uranyl acetate) interfere with the result. The average deviation from the mean is $\simeq$ 5 per cent. K. SAITO

2867. **Determination of calcium and magnesium in mineral waters.** M. Kobrová (*Chem. Listy*, 1954, **48** [8], 1255–1257).—The conditions for the complexiметric determination of Ca and Mg in the presence of relatively large amounts of each other and of Fe and CO_2 have been studied. To determine Ca in mineral waters, treat the sample (50 to 100 g) with Na tartrate (1 to 2 g) to mask Fe, add a known excess of EDTA (disodium salt) (**I**), expel CO_2 by boiling, dilute the soln. with water (250 to 300 ml), add murexide to a pale-red colour, then NaOH (2 g), and titrate the excess of **I** with a standard soln. of Ca^{++}. The end-point is marked by a sharp colour change from violet to red. To determine Mg, dilute a sample of the mineral water (50 to 100 g) with water (300 ml), warm to 60° C and add 5 ml of a buffer (prepared by diluting 54 g of NH_4Cl and 250 ml of 35 per cent. aq. NH_3 to 1 litre) for each 100 ml of the soln., followed by Eriochrome black T and a known excess of **I**. After heating the mixture for a short while to between 90° and 100° C, titrate the excess with Ca^{++}. The Mg content is determined from the difference of the amounts of **I** soln. consumed in the titrations to murexide and to Eriochrome black T. G. GLASER

2868. **Determination of radioactive strontium and barium in water.** R. B. Hahn and C. P. Straub (*J. Amer. Wat. Wks Ass.*, 1955, **47**, 335–340).—A method is described by which radioactive Sr and Ba (discharged into water by nuclear power industries) can be determined at low concentrations with $\simeq$ 10 per cent. precision. After studying concentration methods by evaporation, ion exchange and precipitation, the last was suitably adapted to concentrate radioactive components, evaluate interfering substances (Ca, Mg, Fe, etc.) and determine Sr as $SrC_2O_4.H_2O$ and Ba as $BaCl_2.2H_2O$ by counting the mounted ppt. with a mica end-window Geiger - Müller tube of window thickness 2·3 mg per sq. cm. An analytical technique is described in detail, the essential stages being the pptn. of Sr + Ba as carbonate, dissolution of the ppt. in HNO_3, and pptn. of the nitrates in acetone [$Ca(NO_3)_2$ is soluble]. After treatment of the ppt. with $Fe(NO_3)_3$ and 6 *N* aq. NH_3, Ba is re-pptd. as chromate and Sr as oxalate from the chromate filtration. The ppt. are dried, weighed and counted. The method, tested with a standard HCl tracer solution of ^{90}Sr - ^{90}Y or ^{140}Ba - ^{140}La of known activity, proved to be sensitive for concentrations of Sr of 4×10^{-8} and of Ba of 10^{-7} μC per ml. Different isotopes, *e.g.*, ^{89}Sr and ^{90}Sr, ^{137}Ba and ^{140}Ba, cannot be distinguished by this method and would require further decay and absorption analyses. S.C.I. ABSTR.

2869. **The spectrophotometric determination of nitrate in natural waters, with particular reference to sea water.** J. B. Mullin and J. P. Riley (*Anal. Chim. Acta*, 1955, **12** [5], 464–480).—Nitrate occurs in sea water in concn. of 1 to 600 mg of N per cu. metre. It exercises a controlling influence on marine life, and numerous methods have been proposed for its determination. These methods are reviewed and a new procedure is presented. Nitrate is reduced to NO_2' in alkaline soln. with hydrazine under the catalytic influence of Cu^{++}, and a reproducible but not quant. yield of NO_2' is obtained. The reduction is complete in 24 hr. at room temp. The NO_2' is then determined by the method of Rider and Mellon (*Brit. Abstr. C*, 1946, 150). The reduction is inhibited by as little as 0·0001 per cent. of Mg^{++} at pH 12·1, but adjustment of the pH to $\simeq$ 9·6 with a NaOH - phenol buffer eliminates this interference. Corrections are applied for the Cl′ concn., which adversely affects the reduction, and for any NO_2' originally present and which is partly destroyed in the reduction. The method will detect $\simeq$ 0·3 μg of N, as NO_3', per litre and gives a standard deviation of $\simeq$ 2 per cent. in the range 20 to 600 μg of N as NO_3' per litre. W. C. JOHNSON

2870. **Determination of selenium in sea-water.** M. Ishibashi, T. Shigematsu and Y. Nakagawa (*Records Oceanog. Works, Japan*, 1953, **1**, 44–48).—Add 700 mg of Fe^{+++} to 20 litres of sea water and slowly mix with 20 ml of aq. NH_3 to ppt. $Fe(OH)_3$ as carrier for Se. Dissolve the ppt. in H_2SO_4 and add 15 mg of As^{+++}. Ppt. the As as As_2S_3, which carries down the Se in the ppt. Dissolve the filtered-off ppt. in HBr. Distil off the Se from a mixture of 20 ml of aq. HBr (47 per cent.) and 40 ml of 18 *N* H_2SO_4. Acidify the distillate with HCl, add 1 ml of aq. phenol (1 per cent.) and 5 ml of aq. thiourea (10 per cent.) and dilute to 50 ml. Measure the resulting red colour. The selenium content of Japanese coastal waters ranged from 4 to 6 μg per litre. CHEM. ABSTR.

2871. **Identification of petroleum refinery wastes in surface waters.** A. A. Rosen and F. M. Middleton (*Anal. Chem.*, 1955, **27** [5], 790–794).—The i.r. spectral patterns of the aliphatic and aromatic hydrocarbon fractions separated from the wastes of five refineries were sufficiently characteristic to suggest their use as non-subjective evidence of the presence of low concn. of petroleum refinery wastes in surface waters. *Procedure*—Isolate the neutral fraction from the sample as previously described (*Ind. Eng. Chem.*, 1954, **46**, 284). Dissolve $\gtrsim$ 1·5 g in *iso*octane (4 ml) and adsorb on to a column of silica gel (18 g). Elute in turn with *iso*octane (85 ml) (giving the aliphatic fraction), benzene (85 ml) (aromatic fraction) and $CHCl_3$ - methanol (1:1, 85 ml) (polar fraction). Concentrate each eluate to $\simeq$ 5 ml and record the i.r. spectrum from 5 to 16 μ. The organic matter from three samples of surface water, containing various amounts of refinery wastes, has been examined by this method. It is claimed that the results are a useful supplement to odour evaluations. A. R. ROGERS

2872. **Determination of acetone in sewage waters and other dilute solutions.** Yu. Yu. Lur'e and Z. V. Nikolaeva (*Zavod. Lab.*, 1955, **21** [4], 410–413).—The colorimetric methods for determining acetone based on condensations with salicylaldehyde and with furfuraldehyde are studied. The latter method, due to Chelintsev and Nikitin (*J. Gen. Chem., U.S.S.R.*, 1933, **3**, 319), is the more sensitive and is applied to the determination of acetone concentrations from 1 mg to several g per litre in sewage and other waters. A calibration curve is constructed by means of standard solutions containing from 1 to 20 mg of acetone per litre. Each solution (2·5 ml) is mixed with 0·2 ml of ethanolic furfuraldehyde solution (5 ml of furfuraldehyde in 100 ml of ethanol—the use of an ethanolic solution instead of the aq. solution of Chelintsev and Nikitin increases the sensitivity) and 0·5 ml of NaOH solution (10 g of NaOH in 100 ml of water), and after 30 min. at room temp. 15 ml of 50 per cent. H_2SO_4 (400 ml of conc. H_2SO_4 in 1 litre of solution) are added and the optical densities are determined, using green filters. The molar coeff. of absorption is 14,400. For the analysis of sewage waters a

suitable vol. acidified with H_2SO_4 is distilled until two-thirds of its bulk is collected, 50 ml of water are added to the distillation flask and a similar volume is collected by further distillation. The distillate is made up to a suitable vol. and an aliquot part is taken for determination by the procedure used for obtaining the calibration. Details of volumes employed are not given. Phenol and methanol < 100 mg per litre do not interfere, but formaldehyde gives slightly high results.

G. S. SMITH

2873. **Determination of catechol in industrial waste waters and phenolic products.** J. Janák (*Chem. Listy*, 1954, **48** [8], 1171–1175).—Catechol is determined colorimetrically by measuring the absorption of the yellow complex formed when catechol reacts with ethylammonium molybdate. *Procedure*—To a filtered sample of the waste waters containing 60 to 80 mg of catechol add 10 per cent. aq. Pb acetate (pH ≮ 5·7) at 60° C and pH 6 to 7. Decompose the ppt. of the catechol - lead complex with *N* H_2SO_4. From the filtrate take an aliquot containing 1 to 4 mg of catechol, dilute it with H_2O to 10 ml, add 5 ml of a 5 per cent. soln. of ammonium formate in anhyd. methanol (to stabilise the Mo complex), dilute the soln. to 50 ml with anhyd. methanol, add 1 ml of the reagent (prepared by liberating the free base from 13·2 g of ethylamine hydrochloride with an equiv. amount of NH_3, adding 4·4 g of powdered MoO_3 in the cold, decanting the soln. and diluting it with H_2O to 100 ml) and measure the absorption after 3 to 5 min., using a filter with max. transmittance at 435 mμ. The method, accurate to approx. ± 2 per cent., compares favourably with gravimetric and volumetric procedures.

G. GLASER

2874. **Colorimetric determination of resorcinol in industrial waste waters and phenolic products.** J. Janák and L. Matoušek (*Chem. Listy*, 1954, **48** [8], 1176–1180).—The method is based on the formation of a violet acetone-soluble product by iodination of mixtures of resorcinol with catechol. *Procedure*—Treat the filtered sample of the phenolic effluent (25 ml) with *N* H_2SO_4 to pH 6 to 7, followed by 10 per cent. aq. Pb acetate (15 ml). Filter off the ppt., treat the filtrate with powdered Na_2SO_4 (1 to 2 g), remove the pptd. $PbSO_4$ by filtration and dilute the filtrate to a suitable volume. Take an aliquot containing 50 to 200 μg of resorcinol, mix it with a 0·2 per cent. aq. soln. of catechol (2·5 ml), dilute the soln. to 10 ml, add an acetate buffer (10 ml) [prepared by neutralising a soln. of glacial acetic acid (30 ml) in water (800 ml) with 25 per cent. NaOH (75 ml)], followed by a rapid addition of 0·1 *N* iodine (15 ml). After exactly 1 min., destroy the excess of iodine with 0·1 *N* $Na_2S_2O_3$ (15 ml), dilute the mixture with acetone (50 ml) and measure the absorption on a colorimeter provided with a green filter with light transmittance from 480 to 600 mμ (max. at 520 mμ). The resorcinol concn. (in mg per ml) is given by the expression $\frac{7{\cdot}35\,A - 6{\cdot}62}{ab} \times c$, where A is the percentage light absorption, a the original vol. of the sample, b the vol. of the aliquot, and c the vol. to which the original sample is diluted. To determine resorcinol in phenolic products, dissolve the sample (5 to 10 g) in a little methanol and dilute the soln. to 250 to 500 ml with water. From the filtered soln. take a 25-ml aliquot, dilute it to between 250 and 500 ml, treat 2 to 5 ml of this soln. with 0·2 per cent. aq. catechol, dilute to 10 ml and proceed as above.

G. GLASER

2875. **Determination of phenols in disinfectants for the dairy industry.** G. Wildbrett (*Fette u. Seifen*, 1955, **57** [4], 245–247).—The method is based on the reaction of phenols, chlorophenols and cresols with 2:6-dibromoquinonechloroimine (**I**) in alkaline soln. A series of standard solutions are prepared containing 10, 20, 40, 60, 80 and 100 μg of phenol in 10 ml of a borate buffer soln. (pH 9·0 to 9·6); 0·2 ml of a soln. of **I** (40 mg of **I** in 10 ml of 95 per cent. ethanol) is added to each. After 15 min., the extinction of the blue colour is measured in an Elko-II absorptiometer with 5-mm cuvettes and filter I 62. A blank reading obtained with the reagent in the buffer soln. is subtracted from the phenol readings. Similar measurements are made with suitable dilutions of the disinfectant. For 5 to 100 μg per 10 ml of phenol, *m*-cresol or *p*-chlorophenol, the relationship between the extinction and the phenol concn. is linear, but the absolute extinctions decrease in the order given. Results obtained on commercial disinfectants are expressed in arbitrary "phenol values," based on a phenol standard. The method can be used to check commercial disinfectants and also to determine the concn. of a known disinfectant in soln.

E. HAYES

2876. **The Peet - Grady method: official method of the Chemical Specialties Manufacturers Association for evaluating liquid household insecticides: latest revision.** (*Soap., N.Y.*, 1955, *Blue Book*, 249–250).—Full particulars are given of the Peet - Grady method, first officially adopted in 1932 and subsequently revised.

G. HELMS

See also Abstracts 2798, 2822, 2906.

Agriculture and Plant Biochemistry

2877. **Spectrographic analysis of briquetted unashed plant material.** J. H. Muntz and S. W. Melsted (*Anal. Chem.*, 1955, **27** [5], 751–753).—For rapid emission-spectrographic analysis of vegetable material, use of a compressed briquette or pellet is preferred to techniques involving ashing. The finely powdered sample (150 mg) is prepared by mixing it in an agate mortar with lithium carbonate (75 mg) and graphite (450 mg), and briquetting at 100,000 lb per sq. in. Excitation is by the high-voltage spark. Standard samples are used to prepare working curves. A single exposure suffices to determine B, P, Mn, Li, Mg, Ca, Cu and K with an accuracy of ≃ ± 20 per cent.

A. R. ROGERS

2878. **A modified colorimetric method for the field determination of soil nitrate.** W. R. Horne and O. T. Denmead (*J. Aust. Inst. Agric. Sci.*, 1955, **21** [1], 34–36).—A rapid and simple colorimetric method is described for the field determination of nitrate-N in soil. The method is accurate to 1 p.p.m. *Procedure*—The sample (4 g) of well-broken and mixed soil is leached with Morgan's solution [100 g of sodium acetate (A.R.) in 1 litre of water and 30 ml of glacial acetic acid rendered nitrate-free with powdered Zn (pH 4·8)] to give 10 ml of solution. To a 2·5-ml aliquot, 0·25 ml of a 5 per cent. w/v solution of brucine in glacial acetic acid is added, followed by 5 ml of conc. H_2SO_4. After mixing and allowing to stand for 7 min., the permanent yellow colour developed is matched against the standard discs in a Lovibond tintometer or against

standards prepared from Ilford gelatin photographic filters (yellow No. 104 and 110). A reagent blank is necessary. The results include nitrite-N.

S. C. JOLLY

2879. **The Denigès method for determination of phosphate, with special reference to soil solutions and extracts.** S. H. Yuen and A. G. Pollard (*J. Sci. Food Agric.*, 1955, **6** [4], 223–229).—A modified method involving the reduction of molybdophosphoric acid by $SnCl_2$ is described for the determination of phosphate in soil solutions and soil extracts. The main points considered were: (*i*) the concentration of molybdate, which should be low in order to minimise the effect of silicate, arsenate and $Fe^{\cdots}$; (*ii*) the acidity of the test solution and (*iii*) the concentration of $SnCl_2$. The colour is matched 15 min. after mixing by using a Hilger Biochem absorptiometer (4-cm cell and red filter). With this procedure a linear relationship was established between the phosphate content and the colour intensity for P_2O_5 concentrations up to 2·5 p.p.m. Various ions commonly occurring in soil solutions and some soil extracts did not affect the accuracy of direct determinations of phosphate; $Fe^{\cdots}$ up to 15, and $Fe^{\cdot\cdot}$ up to 200 p.p.m., had no ill effect. Arsenate, which produced a blue colour similar to that produced by phosphate, should be absent from the test.

S.C.I. ABSTR.

2880. **Rapid determination of quartz, potash minerals and plagioclase felspars [in soils, etc.].** E. R. Graham (*Chemist Analyst*, 1955, **44** [2], 37–38).—After removal of Fe, the sample (2 g) is mounted on a microscope slide so that the grains are half-embedded in the cement. The grains are exposed to HF for 1 to 5 min. until etching is adequate, and the slide is then immersed in a saturated soln. of sodium cobaltinitrite for 5 min., rinsed with distilled water and then immersed in 0·1 per cent. aq. malachite green for 5 min., followed by rinsing in distilled water and drying. Quartz grains remain clear and unetched; microcline, orthoclase and mica are coloured yellow by the cobaltinitrite (greenish after treatment with Malachite green), whilst etched aluminosilicates become greenish-blue (albite) or paler and more deeply etched (labradorite). The amount of each mineral can be estimated by comparison with treated slides of known mixtures.

W. J. BAKER

2881. **Modified identification of E605 [parathion] by the azo-dyestuff method.** H. Kaiser and T. Haag (*Dtsch. ApothZtg*, 1955, **95** [9], 211).—The determination of parathion in toxicological specimens by the azo-dyestuff method was affected by the presence of haemoglobin decomposition products in stomach contents, in which blood pigment is liable to mask the parathion dyestuff in alcoholic extracts. The difficulty may be overcome by extracting with benzene, in which the blood pigment is insoluble.

S.C.I. ABSTR.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

2882. **Teflon dishes for use with hydrofluoric acid.** T. J. Sentementes and M. A. De Sesa (*Chemist Analyst*, 1955, **44** [2], 54–55).—For analyses of uranium ores involving decomposition of samples by hot HF, Teflon dishes 1 in. deep and 1·75 in. in diam., machined from 2-in. rod, can be substituted for platinum dishes without loss of accuracy. They are satisfactory at temp. near 200° C.

W. J. BAKER

2883. **Filtration expedient.** C. J. Anderson (*Chemist Analyst*, 1955, **44** [2], 54).—A method of freeing an air-pocket between the apex of a filter-paper and the constriction at the top of the funnel-stem is described. It does not require removal of the filter-paper.

W. J. BAKER

2884. **Device to prevent back-suction in vacuum systems.** G. P. Mathur and S. Mukherjee (*J. Chem. Educ.*, 1955, **32** [4], 216).—This device, to prevent back-suction in reduced-pressure distillations, consists of a mercury layer on a sintered-glass funnel connected to the vacuum pump, thus preventing water or air entering if the vacuum pump fails.

A. LEDWITH

2885. **Centrifuge permitting continuous observation of the spinning tube.** B. B. Marsh (*J. Sci. Instrum.*, 1955, **32** [6], 205–206).—Light passes through slits in the upper and lower centrifuge housing so as to intercept the trajectory of the centrifuge tube. The volumes of the separate phases within the tube can be read directly and continuously during centrifugation.

G. SKIRROW

2886. **Use of polyethylene bottles in centrifuges.** J. Golubow and H. D. Jackson (*Chemist Analyst*, 1955, **44** [2], 54).—Polyethylene reagent-bottles (16 oz.) fit directly into the trunnion cups of large laboratory centrifuges without an adapter and can be used from + 20° C to − 20° C. They are easily cleaned with a detergent and will considerably reduce breakage losses. Other sizes can be adapted.

W. J. BAKER

2887. **Centrifugal laboratory stirrer.** J. Říčica and H. Grünwald (*Chem. Listy*, 1954, **48** [8], 1250).—A glass stirrer, suitable for the agitation of foaming liquids (*e.g.*, fermentation liquors) and for stirring with the simultaneous introduction of a gas, is described and illustrated.

G. GLASER

2888. **Simple apparatus for loading paper strips for chromatography.** C. J. Barker and R. H. Perry (*Chem. & Ind.*, 1955, [21], 588).—Where a solution is chromatographed in several portions to obtain a compact spot containing sufficient material, the delay involved by allowing the solution to dry between each application can be considerably reduced by using a simple equipment in which the paper strips are rapidly dried by a stream of hot air.

S. C. I. ABSTR.

2889. **Automatic cut-off valve for ion-exchange columns.** C. A. Hewitt (*Anal. Chem.*, 1955, **27** [5], 865).—The valve that prevents the liquid level falling below the top of the resin bed comprises an immersion tube fitted with a sinter and arranged so that the sintered end is immersed in the liquid at the top of the column. The stem of the tube passes through a rubber stopper, which fits tightly in the column, and the level of solution above the resin should be about half-way between the bottom of the stopper and the sintered disc. The flow of liquid from a reservoir connected to the top of the tube stops when the liquid added reaches the disc, as a partial vacuum is created above the liquid in the column. The disc also helps to reduce turbulence. A sinter of medium porosity will maintain a column of water about 250 cm in height, and one of fine porosity a column of about 450 cm. The use of the valve, by ensuring automatic cut-off, facilitates

simultaneous handling of a number of columns.
K. A. PROCTOR

2890. **Safety gas-bubbler.** A. Gibaud (*Bull. Soc. Chim. France*, 1955, [5], 624–625).—An efficient safe gas-bubbler is described in which the main vessel carries a ground-glass cylinder into which fits a tube with a slightly smaller tube on its lower end. A still smaller inner tube with a flanged end is held inside this by a number of glass balls. In operation, the gas passes into the lower vessel, forces liquid up past the balls in contact with gas and the gas passes upwards through the tube while liquid returns through the central tube. The amount of absorbing liquid may be varied, and it cannot be sucked back into the system. The device has been used for the absorption of keten in NaOH.
E. J. H. BIRCH

2891. **A flask closure for oxidation and reduction volumetric analysis.** W. Bohm (*Chem. Tech., Berlin*, 1955, **7** [5], 288–289).—The closure device is for analytical processes in which the solution to be estimated is treated with an excess of a reducing agent (SO_2) or, less usual, with an excess of an oxidising agent (H_2O_2 or $KClO_3$), and then, before titration of the reduced or oxidised compound, boiled to expel the excess of agent while bubbling an inert gas (CO_2 or N) through the solution to preclude the influence of extraneous oxidising or reducing agents (in the surrounding air). The device consists of a Jena-glass delivery tube (7 to 8-mm bore) for the inert gas, long enough to dip under the solution, and provided at a point in its length with a pear-shaped bulb which fits the neck of the Erlenmeyer or other flask used; the bulb is formed with 6 to 8 indented channels or flutes which permit the escape of the gas and of the vapours of the boiling solution between the closure and the neck of the flask. After the boiling stage the solution in and on the tube and bulb can readily be washed back into the flask. The device has considerable advantages over the usual rubber-bung closures. It was developed for the estimation of V by titration with $KMnO_4$ solution after reduction of the V^V to V^{IV}. In this method it is preferable to modify the classical method of titrating the boiled reduced solution to a direct pale-reddish end-point (from yellow) by titrating the solution with an excess of the $KMnO_4$ solution to a definite pink and then titrating drop by drop with ferrous sulphate solution to a sharp yellow end-point, which is more easily visible.
H. L. WHITEHEAD

2892. **A micro-distillation apparatus for the fractionation of small amounts of radioactive liquids.** W. Block (*Z. anal. Chem.*, 1955, **145** [6], 424–426).—The distillation flask, containing $\simeq$ 100 mg of sample, carries three necks and a vacuum stopcock. Each neck is fitted with a special combined water-cooled reflux condenser and receiver, which can slide up and down in a rubber bung. Vapour enters the lower end of each condenser through a capillary tube, and the condensate is trapped between the capillary and the water-cooled surface; the upper ends are connected to a vacuum pump. In operation, the sample is refluxed gently under vacuum, with all three condensers high up in their bungs. Then each condenser in turn is slid down to within 1 to 2 cm of the surface of the sample, and a fraction of distillate is collected in the trap. The stopcock permits the passage of a stream of gas through the apparatus instead of the use of vacuum.
A. R. ROGERS

2893. **Versatile automatic fraction collector with new features.** W. F. Guilbeau and E. J. Roberts (*Chemist Analyst*, 1955, **44** [2], 53).—In the device described and illustrated, chromatographic fractions of definite vol. are collected, without loss of eluate, by means of an intermittent siphon during the movement of a 28-in. turntable. The latter is geared so that each 180° rotation of the motor-shaft brings a new collecting tube into position.
W. J. BAKER

2894. **Electronically controlled apparatus for collecting fractions.** M. D. Sorcina (*Chim. Anal.*, 1955, **37** [5], 172–174).—An automatic fraction collector is described in which the mobile phase is collected in a siphon delivering constant volumes. The apparatus is held in position during the time required for a condenser to charge. When the condenser discharges, the apparatus is released, enabling the next collecting tube to come into position.
J. H. WATON

2895. **Automatic fraction collector.** W. C. Lister (*Chem. & Ind.*, 1955, [21], 583–586).—The apparatus described was devised to effect automatic collection of successive samples of eluate from ion-exchange columns or in the course of chromatographic runs. It consists of a turntable carrying a circular rack of 100 collecting tubes in spiral formation, driven from one tube position to the next by a motor controlled by a relay system operated by a siphon on a balance arm carrying a mercury switch; it could also be used with a process timer or a drop counter.
S.C.I. ABSTR.

2896. **Glass-fibre material for preventing bumping.** H. C. Austin, jun. (*Chemist Analyst*, 1955, **44** [2], 56).—Vigorous and smooth boiling, *e.g.*, during wet digestion of plant material, can be ensured by the introduction of 7-mm discs of Vapoglas (an air-conditioning filter material) cut from 0·125-in. sheets with a cork-borer. The discs should first be cleaned with hot $K_2Cr_2O_7$ solution and then rinsed with distilled water; on completion of the digestion the porous discs can be powdered easily with a stirring-rod, thus assuring extraction of absorbed material. No error is introduced even when determining trace elements.
W. J. BAKER

2897. **Liquid - liquid extractors for laboratory use.** H. L. Rosano and J. Valadier (*Peint-Pigm.-Vern.*, 1955, **31** [3], 228–232).—Continuous liquid - liquid and countercurrent extractors are reviewed. (20 references.)
L. A. O'NEILL

2898. **Enhancing visibility of interfaces with polyethylene discs.** B. F. Stimmel (*Chemist Analyst*, 1955, **44** [2], 55).—The junction of two liquid phases of the same colour and refractive index, *e.g.*, water and organic solvent in a separating funnel, can be defined more easily by inserting a polyethylene disc (0·5 cm in diam.) in the funnel so that it will float at the interface of the two liquids.
W. J. BAKER

2899. **Method for extraction of substances from liquid samples.** D. P. Neves and Y. Tavares (*Science*, 1955, **121**, 313–314).—Two simple devices are described that can be substituted for the thimble in a Soxhlet apparatus to enable extraction of liquids heavier or lighter than the solvent to be carried out without special extractors.
H. F. W. KIRKPATRICK

2900. **Automatic countercurrent distributor.** S. Akabori, K. Tani and S. Tsugita (*Japan Analyst*, 1955, **4** [2], 119–126).—The history of the automatic countercurrent distributor is reviewed and the theory and its practical use are discussed. An example of the construction of a distributor comprising 300 unit tubes (Craig *et al.*, "Technique of Organic Chemistry," Vol. III, Interscience Publishers Inc., New York, 1950) is cited, together with precise instruction for use. The ideal and practical efficiencies of separation and the influence of experimental conditions are discussed. Some suggestions are given on the choice of solvent for the separation of several biochemical substances. K. SAITO

2901. **A simple, inexpensive dry-box substitute.** T. J. Clark, P. K. Conn and R. E. Hein (*Chemist Analyst*, 1955, **44** [2], 55–56).—A procedure for protecting the sample and retaining quartz fragments when opening ampoules containing irradiated samples of volatile compounds is described. The quartz ampoule, immersed in solid CO_2 in a 400-ml beaker, is placed in the bottom of a large thin polyethylene bag (loosely tied with soft copper wire), which eventually fills with gaseous CO_2. Opening the ampoule can be done in sight of the operator, and carriers can be introduced by pipettes inserted through the restricted neck of the bag; the diluted sample can be withdrawn similarly.
W. J. BAKER

2902. **Improved Edwards' gas-density balance.** H. E. Hoelscher, R. F. Kayser and R. H. Price (*Chemist Analyst*, 1955, **44** [2], 43–46).—The original Edwards' gas-density balance (*U.S. Bur. Stand.*, 1917, *Tech. Paper* 89) has been modified so as to remove a number of serious disadvantages. Features of the new design are described and shown in a diagram. The accuracy of the improved balance is within ± 0·0001 density unit, and calibration by an independent analytical device is now unnecessary. The balance has been used for such studies as the hydrogenation of propylene in a flow system where many very frequent gas-analyses are necessary.
W. J. BAKER

2903. **Precision density and surface-tension measurements in the sugar factory.** A. Pochan (*Chim. Anal.*, 1955, **37** [6], 201–207).—The principal faults encountered in hydrometers (areometers and areoscopes) are described in detail. Commercially available apparatus is described which permits a rapid determination of density to 5 decimal places. Among the instruments mentioned are a micro-areoscope which requires only 20 ml of liquid, and a capillary tensiometer suitable for estimating the corrections to be applied for surface tension.
J. H. WATON

2904. **Syringe pattern micro-pipette.** British Standards Institution (B.S. 1428: Part D5: 1955, 12 pp.).—Recommended dimensions, etc., for borosilicate-glass syringe pipettes having delivery vol. of 0·25, 0·5 and 1·0 ml, respectively, with a tolerance of ± 0·002 ml, are given. The only mandatory dimension is the diameter of the ground portion of the piston, which must be 6·0 ± 0·1 mm. The upper end of the barrel is joined to a wider tube that is partly cut away to form upper and lower stops for the crook handle of the piston.
W. J. BAKER

2905. **Micrometer-operated burette.** British Standards Institution (B.S. 1428: Part D6: 1955, 12 pp.).—Dimensions and drawings of borosilicate-glass micro-burettes having nominal vol. of 0·5 and 1 ml, respectively, are shown. The barrel and piston are horizontal in use, and the jet is bent over at 90° for convenience in delivery. The piston is connected to the screw-head of a British Standard micrometer having a measuring range of 25 mm graduated in 0·005 mm and accurate to 0·0001 ml. The vol. of liquid delivered by the jet is calculated directly from the micrometer reading. A suitable stand and connection between piston and micrometer are shown. W. J. BAKER

2906. **Electrostatic sampler for dust-laden gases.** G. L. Rounds and H. J. Matoi (*Anal. Chem.*, 1955, **27** [5], 829–830).—An electrostatic sampler that uses a commercially available voltage source and will collect up to 5 times the weight of dust collected by conventional samplers is described. To allow for more uniform deposition the collector is in the form of a truncated cone, and the whole unit can be easily taken apart for cleaning. K. A. PROCTOR

2907. **Controlled water flows.** G. T. P. Tarrant (*J. Sci. Instrum.*, 1955, **32** [5], 191–192).—A controlled variable flow of water over a range 2000:1 is obtained by applying a constant head to a tap consisting essentially of a screw thread. Flow takes place between the male and female parts of the thread. As the male part is withdrawn by unscrewing, water is able to pass through slanting slots milled in the male thread so as to greatly increase the rate at which water can pass when the tap is nearly open. G. SKIRROW

2908. **A new particle-size analyser.** M. E. O'K. Trowbridge (*Ind. Chem. Mfr*, 1955, **31** [363], 195–196).—A new instrument (the Sharples micromerograph) for the determination of particle size is described and illustrated. It depends on the sedimentation of the material through a column of liquid on to the pan of a servo-electric balance, which records data automatically with accurate and reproducible results. The apparatus is simple to operate and reduces the time required for a particle-size distribution analysis of a ≃ 0·1-g sample to 15 min. The instrument can be applied in research and development, production and quality control of any powdered materials, *e.g.*, penicillin for human use, tungsten carbide for cutting tools, and limestone for pigments.
S.C.I. ABSTR.

See also Abstracts 2615, 2626.

Optical

2909. **New fluorescence photometer.** F. J. Lynch and J. B. Baumgardner (*Rev. Sci. Instrum.*, 1955, **26** [5], 435–440).—The unknown and a reference sample of the same constitution are excited by pulsed u.v. radiation, and the resulting light from each sample is directed on to separate photocells. The ratio of the fundamental a.c. components of the photo-electric currents flowing in the two cells is measured automatically by a servo mechanism. Circuit details are given. G. SKIRROW

2910. **Estimation of blood-oxygen saturation. A new cuvette.** C. P. Handforth (*Lancet*, 1955, i [25], 1252–1253).—A simple optical cuvette, consisting of a spiral of polythene tubing, is described and illustrated for use in any photo-electric colorimeter for the oximetry of whole blood. Its capacity is 0·2 ml and it may be used to analyse 0·5-ml samples. Calibration of the instrument, the method

and accuracy are described. The percentage saturation is equal to

$$\frac{D_R - D_S}{D_R - D_O} \times 100,$$

where D_R, D_S and D_O are values of the optical density (D) for the fully reduced sample, the sample on collection and the fully oxygenated sample, respectively. The standard deviation of the method is $\pm$ 4 per cent. Estimations are unaffected by bile pigments or plasma lipids. Errors in the haemoglobin estimations have relatively little effect on the calculated oxygen saturation. When an absolute figure for oxygen content is required, oxygen capacity is estimated by the manometric method of Van Slyke and Neil. O. M. WHITTON

2911. **Light-scattering studies in aerosols with a new counter-photometer.** C. T. O'Konski and G. J. Doyle (*Anal. Chem.*, 1955, **27** [5], 694–701).—A recording light-scattering photometer and electronic particle counter are combined to give a single instrument for the rapid determination of size distribution in aerosols. The limit of sensitivity of the photometer is 3×10^{-11} g per litre of a test aerosol 0·3 μ in diameter. The resolving power of the counter lies within a standard deviation of $\pm$ 8 per cent. in diameter, and the lower limit of sensitivity for single particles is a diameter of 0·3 μ. The production of uniform aerosols from uniform hydrosols by the spray-dry technique is described. Pulse amplitudes of test aerosols 0·33, 0·5 and 1·0 μ in diameter were found to be proportional to the square of the particle diameter. K. A. PROCTOR

2912. **Construction of flame photometer with internal standard.** E. S. Jones and B. Collinge (*J. Med. Lab. Technol.*, 1955, **13** [2], 68–73).—An apparatus is described for the estimation of Na and K. The flame uses coal-gas and compressed air. The burner is surrounded by a Pyrex-glass water-jacket, through which cold water is circulated. The internal standard is Li_2SO_4. A null-point system is used in the measuring circuit. Plasma is diluted 1 in 100 for determining Na, and 1 in 25 for K. F. W. DIGGINS

2913. **A rotating electrode for spectrographic analysis of metallic samples.** C. L. Dotson (*Applied Spectroscopy*, 1955, **9** [1], 33–36).—A method of supporting a disc electrode to present a horizontal sparking surface rotating at speeds up to 5 r.p.m. is described. Improvement from 5 to 1 per cent. in coefficient of variation is claimed for the determination of Sn (0·2 to 2·0 per cent.) and Al (0·07 to 0·2 per cent.) in Zn. Multi-source conditions, line-pairs and rotational speeds are also given for Pb (0·3 to 1·5 per cent.) and Fe (0·005 to 1·5 per cent.). P. T. BEALE

2914. **Use of a 50-cm heated gas cell in ultra-violet spectrophotometry.** W. F. Hamner, N. Hadden and W. M. Padgett II (*Anal. Chem.*, 1955, **27** [5], 747–749).—The bands in the u.v. spectrum of a compound in the vapour phase are often better resolved and at shorter wavelengths than those in the liquid phase. The magnitude of this vapour-solution shift is useful for positive qualitative identification purposes. The construction of a 50-cm heated gas cell for use in such work is described. Heating is accomplished by tape heaters lying along the tube, and the range of temperatures is 25° to 200° C. The housing can be water-cooled at elevated temperatures and is designed to fit the Cary spectrophotometer. K. A. PROCTOR

2915. **New xenon light source for the vacuum ultra-violet.** P. G. Wilkinson and Y. Tanaka (*J. Opt. Soc. Amer.*, 1955, **45** [5], 344–349).—A new light source for the vacuum ultra-violet region is described in which the continuous molecular emission spectrum of xenon is excited by microwave power at a frequency of 2450 Mc. per sec. The source is constructed of Pyrex glass and carries a fluorite window. The useful spectral range is 225 to 150 mμ. B. S. COOPER

2916. **Simple recording attachment for a Beckman DU spectrophotometer.** S. O. Nielsen (*Rev. Sci. Instrum.*, 1955, **26** [5], 516–517).—Simple modifications to the spectrometer circuit are described which enable the unit to be attached to a recorder. A standard (4 sec.) Brown recording potentiometer is connected by means of a simple resistor circuit to a Beckman DU spectrophotometer equipped with a red-sensitive photocell and a blue-sensitive photomultiplier (1P28) to yield an accurate transmission *vs.* time recording apparatus. G. SKIRROW

2917. **The performance of the Perkin-Elmer model 21 in the region 210 mμ to 2000 mμ.** V. Coates, T. Miller and A. Savitzky (*Applied Spectroscopy*, 1955, **9** [1], 14–19).—The conversion of a standard infra-red recording spectrophotometer to permit the measurement of absorption spectra in the region 0·2 to 2·0 μ is described. Hydrogen-arc (0·2 to 0·35 μ) and tungsten-lamp (0·35 to 2·5 μ) sources are interchangeable with the Nernst glower (2 to 15·5 μ) and a fused-silica prism is used. An 1P28 photomultiplier tube for the lower and a lead sulphide cell for the intermediate wavelength range replace the thermocouple used in the infra-red region. Examples of the performance of the instrument are given. P. T. BEALE

2918. **Automatic electronic polarimeter.** G. F. Landegren (*Rev. Sci. Instrum.*, 1955, **26** [5], 502–504).—A light-beam, after passing through a continuously rotating Polaroid disc, is divided into two beams, one of which passes through the sample. Each beam then passes through separate Polaroid elements and falls on separate photocells. The output of each photocell is amplified and fed to an electronic phase meter, in which the angular phase displacement produced by the sample is indicated. G. SKIRROW

Thermal

2919. **Semi-micro calorimeter.** E. Hutchinson and K. E. Manchester (*Rev. Sci. Instrum.*, 1955, **26** [4], 364–367).—The calorimeter described is surrounded by an evacuated space to minimise heat losses. The temp. element is a platinum resistance thermometer. A precision of 0·08 per cent., based on the heat of solution of NaCl, is claimed. The surface energy of NaCl, calculated from data obtained with coarse and with finely divided samples, is 366 ergs per sq. cm. G. SKIRROW

2920. **A 27° C isothermal calorimeter.** P. A. Giguère, B. G. Morissette and A. W. Olmos (*Canad. J. Chem.*, 1955, **33** [4], 657–664).—The construction of a simple Bunsen-type isothermal calorimeter operating as near as possible to 25° C is described; diphenyl ether is used as the working substance. Electrical calibration of the instrument, by comparison with an ice calorimeter, gives a constant of

19·01 ± 0·02 g-cal. per g of Hg, and the *d* of the solid at its m.p. is estimated to be 1·188 g per ml. Heat quantities up to 600 g-cal. can be measured, with a reproducibility of 0·2 per cent., with no temp. drift and a sensitivity greater than 3 times that of the ice calorimeter. G. R. WHALLEY

2921. **Determination of impurity with the melting-temperature apparatus of Smit.** L. T. Carleton (*Anal. Chem.*, 1955, **27** [5], 845–849).—The apparatus of Smit (*Chem. Weekbl.*, 1939, **36**, 750) has been used for the quant. evaluation of impurity in samples (< 0·5 g) by the determination of the melting-temperature curve. Results are probably accurate to within 10 to 30 per cent. of the total impurity as determined by tests on synthetic samples. K. A. PROCTOR

2922. **Binding posts for heating-elements of combustion trains.** Q. Quick (*Chemist Analyst*, 1955, **44** [2], 55).—The one-piece binding post illustrated has cooling fins which ensure that surfaces in contact with the heating element remain cool and free of oxide films. W. J. BAKER

Electrical

2923. **Apparatus for determining electroconductivity.** N. I. Vorob'ev (*Zavod. Lab.*, 1955, **21** [4], 499–500).—Apparatus for determining conductivity with direct current is described. The influence of polarisation at the electrodes, etc., is eliminated by taking the difference of two readings, one corresponding to the passage of electricity through a single column of liquid and the other to its passage through this and another column in parallel. G. S. SMITH

2924. **Studies on controlled potential electrolysis. VI. Construction of a sensitive automatic instrument.** M. Ishibashi and T. Fujinaga (*Japan Analyst*, 1954, **3** [2], 96–98).—A new sensitive potentiostat was designed with the aid of a reversible motor, regulated by a galvanometer switch. The regulating circuit is sensitive enough to detect a potential change of ± 7 mV, allowing a current < 10 mA to flow. The polarisation of the indicator electrode and the internal resistance of the circuit are both negligible. This apparatus can be used for the electrolytic analysis of Cu in the presence of Bi and Pb, and of Ni in the presence of Zn. K. SAITO

2925. **Some applications of the silver-amalgam electrode in oscillographic polarography.** D. Papoušek (*Chem. Listy*, 1954, **48** [8], 1251–1252).—A stationary silver-amalgam electrode replaces with advantage the vibrating silver-amalgam or the mercury electrode. In ammoniacal solutions of chlorides it gives stable and reproducible oscillograms. G. GLASER

2626. **New reference electrodes in polarography.** L. Jensovský (*Chem. Tech., Berlin*, 1955, **7** [3], 159–161).—In polarographic determinations, where the limiting current value and not the half-wave potential is being measured, it is advantageous to replace the calomel and mercury sulphate electrodes by other reference electrodes, such as Sb, Bi, Mo, W and graphite. Such electrodes are pH-dependent and simplify the design of the polarographic vessel. The graphite electrode has a small electrical resistance. Its potential is reached very slowly and is reproducible with difficulty. These electrodes give excellent polarographic waves and the height varies only within the usual limits of error. R. J. MAGEE

2927. **Improvements relating to reference-electrode units.** J. Jackson (Brit. Pat. 729,575, Date Appl. 3.9.53).—An improved reference-electrode unit comprises a calomel electrode sealed in a chamber of which at least a portion projects into a bridge-soln. container. A leakway in the form of a porous plug connects the two. At the base of the bridge-soln. container a second porous plug constitutes a bridge-soln. passage-way. Its resistance to liquid flow is such that a head of 1 ft. of water produces a rate of flow from 0·02 to 2 ml per hr., whilst the resistance of the leakway from the electrode compartment is at least twice this value. Errors due to streaming potential and ohmic drop at the electrode leakway and at the bridge-soln. passage-way are negligible, and the flow of test soln. into the salt bridge is prevented. J. H. WATON

2928. **An apparatus for paper electrophoresis.** G. T. Franglen, N. H. Martin and J. D. Treherne (*J. Clin. Pathol.*, 1955, **8** [2], 144–149).—An apparatus designed to give highly reproducible electrophoretic separation of mixtures is described in detail. Chief features of the apparatus are stable electrical conditions, stable conditions in and about the paper strip, and a means of applying the material for analysis with minimal disturbance of conditions within the cell. H. F. W. KIRKPATRICK

2929. **A modified method of filter-paper electrophoresis.** H. Zentner (*Nature*, 1955, **175**, 953).—An effective method of separating enzyme mixtures, or protein fractions from wheat gluten, involves the use of paper electrophoresis with Cellophane-covered strips (60 cm × 2·5 cm) of Whatman 3 MM paper wrapped spirally round a glass tube through which cold water flows. The tube is partly enclosed in a wooden box lined with buffer-saturated filter-paper; the ends of the long strip pass through two narrow slits and dip into the buffer solutions (with carbon electrodes) below each end of the box. The sample is placed on a marked line on the strip (painted previously with the buffer), and from 9 to 15 V per cm are applied for ≃ 24 hr. to obtain sharp definition of the spots. Full operating details are given. W. J. BAKER

ERRATA.—January (1955) issue, abstract 166, penultimate line.
For "up to" *read* "more than."

September (1955) issue, abstract 2481, line 16.
For "non-graphic" *read* "non-graphitic."

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångstrom unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher -e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
critical	crit.
crystalline	cryst.
crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c.p.s.
decompos -ing, -ition	(decomp.)
density	ρ
density, relative	d or wt. per ml
derivative	deriv.
dilute	dil.
direct current	d.c.
distilled	dist.
electromotive force	e.m.f.
electron-volt	eV
equivalent	equiv.
experiment	expt.
foot, feet	ft.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
horse-power	h.p.
hour	hr.
hydrogen ion concentration	$[H^{\cdot}]$
hydrogen ion exponent	pH
inch	in.
infra-red	i.r.
insoluble	insol.
kilogram	kg
kilovolt	kV
kilowatt	kW
maxim -um, -a	max.
melting-point	m.p.
microcurie	μC
microgram	μg
microlitre	μl
micron	μ
milliampere	mA
millicurie	mC
milligram	mg
millilitre	ml
millimetre	mm
millimicron	mμ
millivolt	mV
minimum	min.
minute (time)	min.
molar (concentration)	M
molecul -e, -ar	mol.
normal (concentration)	N
number	no.
observed	(obs.)
ounce	oz
part	pt.
patent	pat.
parts per million	p.p.m.
per cent. wt. in wt.	per cent. w/w
per cent. wt. in vol.	per cent. w/v
per cent. vol. in vol.	per cent. v/v
potential difference	p.d.
pound	lb
precipitate	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ
relative humidity	R.H.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda$
square centimetre	sq. cm
standard temperature and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition the following symbols are used—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicles are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, *e.g.*, $Cu^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, Cl', SO_4''. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, *e.g.*, ferric iron becomes Fe^{III} and cuprous copper Cu^{I}.

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